University of Alberta

Extraction of Hydrocarbons from Drilling Waste Using Supercritical Carbon Dioxide

by

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ABSTRACT

In this research, supercritical fluid extraction with carbon dioxide is investigated for the treatment of a synthetic-based centrifuge underflow drilling waste. The process has been optimized with respect to mixing speed, vessel outlet design, initial waste mass, and the use of additives.

The conditions which yield the best extraction efficiency and the least processing issues, such as solids carryover and system clogging, are treating 50 g of waste at 14.5 MPa and 40°C. The extraction was completed with a new, Teflon® vessel outlet design and a waste additive. The in-vessel mixer was operated at 50 rpm. Carbon dioxide was supplied from the pumps at 28.9 to 38.5 $g \cdot min^{-1}$. The treated waste hydrocarbon content was 0.4%, which is below Canadian regulatory guidelines for environmental release.

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LIST OF ABBREVIATIONS

AE	–	Alberta Environment
AFRD	–	Agriculture, Food and Rural Development
BTEX	–	Benzene, toluene, ethylbenzene, and xylene
CCME	–	Canadian Council of Ministers of the Environment
CNLOPB	–	Canada-Newfoundland and Labrador Offshore Petroleum Board
CNSOPB	–	Canada-Nova Scotia Offshore Petroleum Board
CO_2	–	Carbon dioxide
ERCB	–	Energy Resources Conservation Board
GC/FID	–	Gas chromatography/Flame ionization detection
NEB	–	National Energy Board
NIST	–	National Institute for Standards and Technology
PAH	–	Polycyclic aromatic hydrocarbon
P_c	–	Critical pressure
SCF	–	Supercritical fluid
SC CO_2	–	Supercritical carbon dioxide
SFE	–	Supercritical fluid extraction
SRE	–	Solids removal efficiency
T_c	–	Critical temperature

CHAPTER 1 - INTRODUCTION

Chapter 1 will present the problem definition and objectives of this research project (Section 1.1) and will outline the organization of this thesis (Section 1.2).

1.1 Problem Definition and Objectives

In rotary drilling for petroleum resources, drilling fluids are necessary to clean the well bore and lubricate the drill bit. Non-aqueous based fluids, either synthetic- or oil-based, are necessary for challenging drill operations such as deep or deviated wells because these fluids have higher chemical stability and natural lubricity [1-3]. They are, however, expensive to use (\$250 to \$2500 per m^3) [1] and the wastes that are generated from their use must be properly handled, treated, and disposed of to prevent environmental contamination.

Since 2000, Canadian oil and gas producers have drilled an average of 22,203 wells per year [4]. Offshore, roughly 10% of wells are drilled using hydrocarbon-based drilling fluids [5]. Extrapolating this percentage to onshore operations, this translates into roughly 4.6 million litres of hydrocarbon contaminated waste that must be disposed of, using a rough rule of thumb of 105 L of drilling waste per meter of well drilled and an average depth of 2000 m [1, 6-8].

Regulations in Canada prevent the direct release of these wastes into the environment above certain limits. Offshore operations in Nova Scotia and Newfoundland are not allowed to release any oil-contaminated waste but are allowed to release synthetic-contaminated waste with up to 6.9 g of hydrocarbon per 100 g of waste, providing the operators have demonstrated that reinjection is not feasible [9]. In Alberta, land treatment tends to be the regulators' preferred treatment method for hydrocarbon based drilling waste [10], although alternative methods can be approved providing they meet certain criteria. These alternative methods include reinjection, inerting, bioremediation, and thermal treatment.

Supercritical fluid extraction (SFE) is an alternative treatment method that is currently being researched. The treatment process in this method involves the use of a pure substance as a solvent that is above its thermodynamic critical pressure (P_c) and temperature (T_c). Above the critical point, the gas and liquid phases of the substance merge, producing a supercritical fluid with favourable properties intermediate of both gas and liquid. Properties of a supercritical fluid include a gas-like diffusivity and viscosity and a liquid-like density [11-14]. Additionally, supercritical fluids have a near zero surface tension [14, 15]. The aforementioned properties allow for a very efficient mass transfer of the compound to be extracted into the bulk supercritical fluid. Supercritical fluid technology has already been successful commercially, most notably for the decaffeination of coffee and tea [16, 17]. If carbon dioxide (CO_2) is used as the fluid, it is safer and more economical than traditional liquid solvents [16, 17].

Several lab and pilot scale studies have already been undertaken to investigate the use of various supercritical fluids for the extraction of a variety of hydrocarbons from drill cuttings and fine waste material [18-26]. In these studies, the pressure and temperature of the processes was altered to determine the optimum process conditions. All of the studies reported positive results including very high extraction efficiencies (>98 %). They also concluded that the hydrocarbon, which is recovered following depressurization, is unaltered by the process and could potentially be reused in future drilling operations.

Two studies have previously been undertaken at the University of Alberta in the Department of Civil and Environmental Engineering [21, 22] investigating the use of supercritical carbon dioxide (SC CO_2) for the removal of diesel from drilling waste. The latter study served as the starting point for this research; the determined optimum process conditions were 14.5 MPa and 40°C (from a tested range of 8.96 to 15.2 MPa and 40 to 60°C) using a ribbon blender at 800 rpm and a CO_2 flow rate of 9.6 to 11.6 $g{\cdot}min^{-1}$ [21]. The latter of the studies also determined the importance of mixing to ensure good contact between the supercritical fluid and the waste [21].

Although the results of the previous studies were encouraging, nearly all of them noted certain problems that would prevent easy scale-up of the process. The objectives of this research are, therefore, to further investigate and optimize the application of SFE with CO_2 to the treatment of drilling waste. Specifically, the goal of this research was to apply the previously determined optimum conditions to a different drilling waste and optimize the process by altering mixing speed, vessel outlet design, waste quantity, and waste texture using additives. The goal of the research is to achieve a lab scale SFE system that can be easily applied to different types of drilling wastes while solving the process problems described in previous studies.

1.2 Thesis Organization

The body of this thesis is divided into four main chapters. These are:

- *Chapter 2 – Background Information.* Chapter 2 includes a discussion on the source, quantity and character of drilling waste; the regulations governing the treatment and disposal of these wastes within Canada; drilling waste treatment technologies; supercritical fluid theory and extraction applications, including the removal of hydrocarbons from soil; and previous studies completed on the removal of hydrocarbons from drilling waste using SFE.
- *Chapter 3 – Materials and Methods.* Chapter 3 describes the materials and methods used in this investigation, including the drilling waste sample, the laboratory consumables, the SFE system set up, the SFE procedure, and the total petroleum hydrocarbon analysis procedure.
- *Chapter 4 – Results and Discussion.* Chapter 4 presents a summary of the extractions completed during this study and discusses the pertinent results. Results and discussion are also given for quality control parameters.
- *Chapter 5 – Conclusion and Recommendations.* Chapter 5 summarizes the main research outcomes in light of the study objectives and provides recommendations for future work.

CHAPTER 2 - BACKGROUND INFORMATION

2.1 Characterization of Drilling Waste

The following sections detail the source, quantity, and quality of drilling waste. The background information begins with a general description of rotary drilling and discusses the use and types of drilling fluids (Sections 2.1.1 and 2.1.2). These fluids, and the cuttings from the drill hole, eventually form the bulk of drilling waste, as discussed in Sections 2.1.3 and 2.1.4.

2.1.1 Rotary Drilling and Types of Drilling Fluids

Drilling fluids, or "muds", are a necessary part of rotary drilling for petroleum resources. They consist of a continuous fluid phase in which additives are incorporated to control the fluid properties [3, 27]. During drilling, the fluids are pumped from a storage tank down the drill pipe to the drill bit. Here, they collect the cuttings from the bit and transport them up the annulus between the drill pipe and the borehole wall [27]. Additional functions of drilling fluid include: cooling and lubricating the drill bit and drill string, forming a filter cake to seal and maintain the walls of the borehole, reducing friction in the hole, preventing formation damage, preventing blowouts, preventing lost returns by controlling the pressure on the annulus, preventing the settling of cuttings and therefore preventing stuck drill pipe in the event of a rig shut down, and protecting surrounding formations so that the well may be later surveyed using well logging methods [1-3]. Figure 2.1 shows the circulation of drilling mud on a drilling rig. The shale shaker shown in the figure is discussed later in this section.

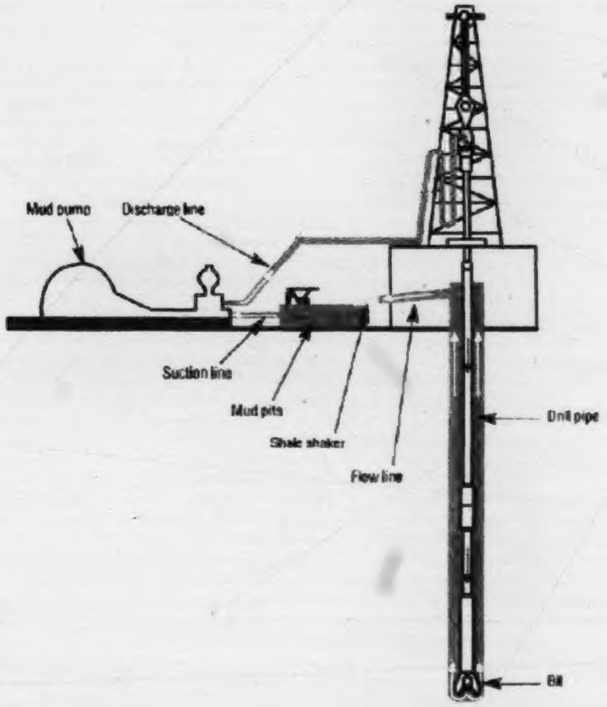


Figure 2.1 Drilling rig showing the circulation of drilling fluid, adapted from [1]

Drilling fluids were first used for rotary drilling in the late 19th century [27, 28]. At that time, water and finely ground drill cuttings were used as the drilling fluid; later, barite and iron oxide were added to control the density of the fluid [28]. By the 1930s, bentonite clays had been added to the fluid to suspend the barite. This bentonite-barite formulation is the base of the drilling muds used today [28].

There are two main, broad classifications of drilling fluid: water-based fluid and non-aqueous-based fluid [3]. Modern water-based fluids consist of a continuous water phase mixed with bentonite clay and barite [2, 3]. While they may be inexpensive [1, 2] and environmentally friendly [29] compared to their non-aqueous counterparts, water-based fluids do have many limitations when it comes to well drilling and completion. Naturally, water-based fluids are less lubricious and therefore not suitable for challenging drilling operations such as deep, deviated or horizontal wells [2, 3]. They also have a higher reactivity with clay and shale, which can cause destabilization of the well bore during drilling [2].

Non-aqueous-based fluids consist of either oil- or synthetic-based fluids. According to Melton et al. [3], oil- or synthetic-based fluids may be categorized by the concentration of aromatic hydrocarbons that contribute to toxicity. "Group 1" contains oil-based fluids with the highest aromatic content (up to 25%) and a polycyclic aromatic hydrocarbon (PAH) concentration greater than 0.35% [3]. "Group 1" fluids usually contain diesel or mineral oil as the continuous phase [3]. "Group 2" fluids have a mid-range aromatic content between 0.5 and 5% and a PAH content between 0.001 and 0.35% [3]. Generally referred to as "low-toxicity mineral-oil-based-fluids", "Group 2" fluids were developed to address the toxicity concerns of "Group 1" fluids [3]. "Group 3" fluids are characterized by both a PAH and aromatic content of less than 0.5% [3].

Non-aqueous-based fluids offer several advantages over water-based fluids. Because they have a higher natural lubricity, they are suitable for challenging drill operations where there is a greater risk of stuck drill pipe [1-3]. Their greater thermal stability makes them less susceptible to boiling and decomposition in deep wells [1-3]. Non-aqueous-based fluids are less reactive in the presence of water sensitive formations and therefore prevent hole enlargement and produce a smaller volume of cuttings [1, 3]. However, non-aqueous-based are much more costly than water-based fluids [1-3] and have a much greater potential environmental impact [1, 3].

Drilling mud technology continues to adapt to meet the need for a more environmentally friendly product. Synthetic-based fluids were developed to be a more biodegradable and less toxic alternative to oil-based fluids, while still providing the technological advantages to drilling with an oil-based fluid [1-3, 5, 30]. With reduced toxicity compared to oil-based fluids, synthetic-based fluids improve safety for the drill crew and reduce the cost of treatment and disposal [5]. Unfortunately, their initial cost is very prohibitive [1, 5]; it can exceed that of oil-based fluids by four or five times [1, 5].

2.1.2 Drilling Fluid Additives

In addition to the basic fluid components presented in Section 2.1.1, drilling fluids contain a number of other additives to control their properties and drilling performance. The choice of additives used is dependent on the subsurface geology encountered when drilling; however, the main additive classes listed here [2, 31]:

- *Weighting materials* – counter the pressure of formations by increasing the density of the mud. Generally, barium sulphate (barite) is used but hematite and lead compounds may be substituted.
- *Corrosion inhibitors* – protect pipes and metallic equipment from acidic formations (containing CO_2, hydrogen sulphide, or oxygen). Generally, iron oxide, aluminum bisulphate, zinc carbonate and zinc chromate are used.
- *Dispersants* – break large solids to small particles to be carried by the fluid. Commonly iron lignosulphates are used for this purpose.
- *Flocculants* – agglomerate suspended particles in the mud so they may be removed efficiently by the solids control equipment (refer to Section 2.1.3). These include salt, hydrated lime, gypsum sodium tetraphosphates, and acrylic polymers.
- *Surfactants* – defoamers and emulsifiers; fatty acids and soaps are often employed.

- *Biocides/Bactericides* – kill microorganisms that form hydrogen sulphide gas. Organic amines, chlorophenols, formaldehydes, sodium hydroxide, and calcium carbonate are often used in this application.
- *Fluid loss reducers* – prevent the loss of drilling mud to low pressure and permeable formations; include starch and organic polymers.

2.1.3 Solids Control

The drilling fluid and cuttings that are circulated from the drill bit to the surface of the well are known as mud returns. Mud returns are processed to remove the cuttings so that the fluid can be recirculated in drilling. Separation of the cuttings is achieved through mechanical separation techniques known collectively as solids control. Properly designed solids control systems better maintain the properties of the mud, reducing the need for costly dilution and chemical treatments prior to recirculation. Solids removal systems generally consist of shale shakers, sand traps, hydrocyclone desanders/desilters, and centrifuges [27].

Shale shakers are the initial and primary method of solids control and are absolutely necessary to protect the downstream solids control equipment [27]. In their basic design, the shakers impart a vibratory motion to a mesh screen that allows the mud returns to pass over it [27]. Mud and particles smaller than the screen openings fall through where they are collected for further processing. Particles larger than the screen openings are collected as waste.

The sand trap (or shale tank) serves as secondary method to remove larger cuttings from the mud returns and protect the downstream equipment [27]. The sand trap operates by allowing larger particles to settle via gravity to the bottom of the tank while collecting the mud and fine particles over a weir [27].

Hydrocyclones operate according to centrifugal forces developed by the tangential velocity of the slurry entering the hydrocyclone body (refer to Figure 2.2) [27]. The incoming mud mixture flows in a downward spiral, along the wall of the cone, and finally to the underflow opening. Here the lighter liquid portion of the stream reverses axial direction and spirals upwards to exit at the overflow opening. The solid particles, due to their heavier mass, exit the underflow opening as the liquid stream reverses upwards.

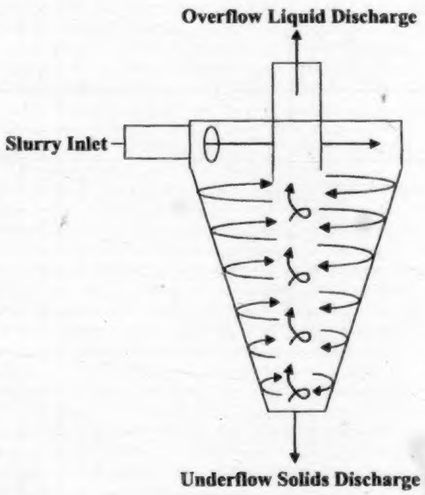


Figure 2.2 Hydrocyclone design, adapted from [27]

Centrifuges are the final step in solids control: they are used to mechanically separate liquids and fine solids [27]. They operate on the same principle as hydrocyclones; however, the centrifugal force is supplied by the centrifuge as opposed to the inlet slurry velocity [27]. Figure 2.3 shows a basic centrifuge design. As the slurry enters the centrifuge, the spinning motion forces it outwards. The solids separate and form a cake against the wall of the centrifuge because of their heavier mass. The blades of the centrifuge move them towards the solids discharge. The liquid collects and drains out the opposite end of the centrifuge.

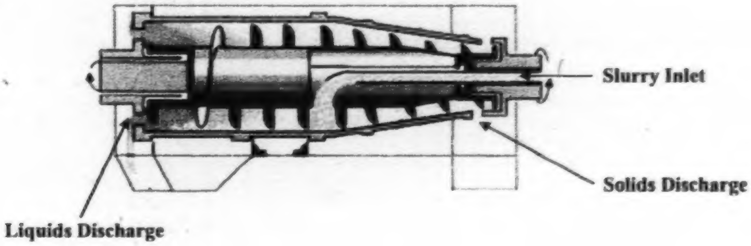


Figure 2.3 Centrifuge design, adapted from [32]

2.1.4 Drilling Waste: Quantity and Character

The spent drilling fluid and the solids discharged from the shale shakers, sand traps, hydrocyclones, and centrifuges are collectively known as "drilling waste". The quality and quantity of waste produced is a function of well diameter and depth; the efficiency and type of solids control; the mud formulation, including the type of base fluid and additives used; and the well subsurface, including the types of formations (i.e. clay, shale) and their contents (i.e. water, oil, gas). The primary waste product generated during drilling is the drilling fluid-contaminated rock cuttings [33]. The waste volume may also contain such items as oil-contaminated rain water, wash water from cleaning the shale shakers, and other non-recyclable fluids used in the drilling process [33].

In terms of quantity, the amount of drilling waste generated may be approximated using the a general guideline of 105 to 1040 L of waste generated per vertical meter drilled [2, 34] or the following equations [1]. First, the volume of cuttings produced is determined based on the volume of the hole drilled:

$$V_{cuttings} = \pi r^2 d \,, \tag{1}$$

where $V_{cuttings}$ is the cuttings volume in m^3, r is the wellbore radius in m, and d is the well depth in m.

Because of its reactivity with clays and shales and subsequent hole enlargement, water-based mud requires a 'washout factor' of 15 to 20% to be applied to Equation (1). The total volume of mud required to drill the well may be determined using Equation (2).

$$V_{mud} = \left(V_{cuttings}\right)\left(1 - \frac{SRE}{100}\right)\left(\frac{1 - F_{drill\ solids}}{F_{drill\ solids}}\right), \tag{2}$$

where V_{mud} is the total volume of mud required to drill the well in m^3, $V_{cuttings}$ is determined from Equation (1); SRE is the solids removal efficiency of the solids control equipment in percent; and $F_{drill\ solids}$ is the fraction, by volume, of the cuttings remaining in the mud after solids control.

Typically, the SRE is 60 to 80% for water-based fluids and may be up to 95% for non-aqueous based fluids [1]. The fraction of drill solids in the mud generally ranges from 0.03 to 0.05 for water-based fluids and 0.08 to 0.10 for non-aqueous based fluids [1].

Drilling waste, then, is a very significant waste stream in terms of volume. For example, a typical offshore well in Canada is 5000 m in depth and 311 mm in diameter

[1, 7]. Assuming a non-aqueous mud is used, a SRE of 80%, and a fraction of drill solids in mud of 0.09, the total amount of waste produced would be approximately 1146 m^3. This figure includes 380 m^3 of cuttings and 766 m^3 of base fluid [1, 5]. Although the non-aqueous base fluid is often reused from well to well, eventually it must also be disposed of.

2.2 Treatment and Disposal of Non-Aqueous Drilling Waste

Petroleum exploration and drilling within Canada occurs both on- and off-shore. Each presents its own challenges for the treatment and disposal of hydrocarbon contaminated drilling waste. In Canada the laws regarding drilling wastes are handled provincially. In the following sections, the pertinent regulatory bodies and legislation for drilling waste disposal in Canada are identified. A general overview is provided for offshore regulations while the emphasis for onshore regulations is placed on Alberta drilling operations.

2.2.1 Canadian Regulations, Offshore

Offshore drilling in Canada occurs mainly in the territorial waters of Newfoundland and Nova Scotia; however, offshore exploratory drilling also occurs in British Columbia and the Arctic [8]. Offshore drilling in Newfoundland and Nova Scotia is regulated through the Canada-Newfoundland and Labrador Offshore Petroleum Board (CNLOPB) and the Canada-Nova Scotia Offshore Petroleum Board (CNSOPB). These boards were created by joint parliamentary acts between the provincial and federal governments and their environmental responsibilities are dictated therein [35-38].

Frontier petroleum resources (such as those in offshore British Columbia and the Arctic) are regulated by the National Energy Board (NEB) whose environmental responsibilities are prescribed by the *Canada Oil and Gas Operations Act* [39].

The *Offshore Waste Treatment Guidelines* is a joint document from the NEB, CNLOPB and CNSOPB which provides instruction on the handling of waste products from offshore facilities [9]. As stated within the *Guidelines*, no wastes generated while drilling with oil-based mud are allowed to be discharged directly to the sea and a treatment and disposal plan for these wastes must have approval prior to drilling. The plan may include transporting the wastes onshore for treatment and disposal. Wastes generated from synthetic-based mud and enhanced mineral oil-based mud are permitted to be discharged to sea providing that reinjection (refer to Section 2.2.3.2.1) can be proven impractical and the hydrocarbon content is less than 6.9 g of hydrocarbon per 100 g of waste.

2.2.2 Canadian Regulations, Onshore (Alberta)

As previously mentioned, this section will focus entirely on the drilling waste regulations of the province of Alberta. The purpose of this is for brevity (as each province is free to set its own regulations) and due emphasis as Alberta produces 68% of Canada's crude oil and 70% of Canada's natural gas [40].

2.2.3 Treatment and Disposal Options under Alberta Regulations

In Alberta, the treatment and disposal of non-aqueous drilling wastes is regulated in *Directive 050: Drilling Waste Management* (previously *Guide 50*) [10]. Prepared jointly by the Energy Resources Conservation Board (ERCB), Alberta Agriculture, Food and Rural Development (AFRD) and Alberta Environment (AE), this directive provides an overview into the on- and off-site disposal methods, notification and approval requirements, sampling methods and toxicity assessments for drilling waste [10].

Non-aqueous drilling waste, due to its inherent higher toxicity and environmental risk, has much fewer disposal options that its water-based counterpart. In *Directive 050*, the ERCB allows hydrocarbon based drilling waste to be disposed of via land treatment or alternative disposal methods, discussed in the following sections [10].

2.2.3.1 Land Treatment of Non-Aqueous Based Drilling Waste

According to the ERCB, land treatment involves the incorporation of the drilling waste into the soil of a dedicated waste site over the long term. The site is managed in such a way to allow the waste constituents (i.e. hydrocarbons) to be biodegraded [10]. The basic concept of land treatment involves spreading the waste on a dedicated parcel of land, incorporating the waste into the soil, adding amendments (such as fertilizer) as necessary, and monitoring soil quality [10, 41-43].

Prior to using land treatment as a waste disposal option, a detailed disposal plan must be submitted to the appropriate regulatory agency. On private lands, approval is handled by the ERCB and its associated field offices. On public lands in settled areas, the AFRD handles approval; on private lands in unsettled or forested regions, AE is responsible for approvals [10]. The submitted disposal plan must include detailed information on the type of drilling fluid used, concentration of salts and additives in the fluid, proposed location for disposal including topography and soil strata, proposed waste application rate, and proposed tillage and amendment addition schedules [10].

The hydrocarbon and salt content of the soil must be monitored before and during land treatment. Closure of the site is achieved once the subsoil hydrocarbon content is below 0.1% dry weight or the topsoil hydrocarbon content is below 0.5% dry weight [10]. The electrical conductivity, measured in $dS\cdot m^{-1}$, provides a measure of the salt or ion concentration. For site closure, the conductivity of the subsoil must be less than 4 $dS\cdot m^{-1}$; the electrical conductivity of the topsoil must be less than 2 $dS\cdot m^{-1}$[10].

Land treatment of oil-based drilling waste is a proven technology which has been successfully applied for decades [41-48]. For example, a study was undertaken by Amoco Canada Petroleum [41] to determine a successful land treatment technique at 33 drill sites within the west central area of Alberta. The soil strata in the area are glacial in origin: typically a shallow layer of weathered topsoil underlain by clay and occasional sand and gravel layers [41]. Approximately 2 acres of land at each of the sites was dedicated to land farming. Depending on the well drilled and the actual site size, drill cuttings were applied at an average rate of approximately 183.5 $m^3\cdot acre^{-1}$, which is equivalent to a layer about 4.5 cm deep [41]. At the time of the study, Amoco Canada Petroleum used an oil-based mud system with a one-to-four ratio of 200,000 $mg\cdot L^{-1}$ $CaCl_2$ brine to No. 2 diesel fuel. The mud also contained emulsifiers, surfactants, and lime [41]. After the collection of the mud through standard solids control methods, the remaining contaminated cuttings were spread as thinly as possible over the treatment area using a bulldozer. Previously stripped topsoil was tilled into the cuttings followed by a high-nitrogen fertilizer at an average application rate of 454 $lb\cdot acre^{-1}$ [41]. Tilling and fertilizing was completed 2 to 3 times per year, depending on results of yearly soil samples. Each of the sites was sampled in either 30 or 60 locations to a maximum depth of 45.7 cm. Although the intent of the study was to reduce the hydrocarbon content of the drilling waste, samples were also analyzed for pH, electrical conductivity, and chlorides, among others [41]. Once the hydrocarbon content of the soil dropped below 2%, the site was given a final cultivation and was sown with grass seed [41].

At the site reported with the highest initial level of contamination a reduction in hydrocarbon content from 7.37% to 1.45% was observed in the surface layer of soil in the first year [41]. After 3 years, the hydrocarbon content had been further reduced to 0.58% [41]. In a similar manner, the electrical conductivity was reduced from 66.7 $dS{\cdot}m^{-1}$ to 11.4 $dS{\cdot}m^{-1}$ in the first year and 1.9 $dS{\cdot}m^{-1}$ after 3 years [41]. The samples taken from the various sites also allowed the study authors to conclude that the hydrocarbons were not migrating off site or leaching into the groundwater.

While the study [41] showed that land treatment was a viable option for the treatment of oil-based drill cuttings, Zimmerman and Robert also share some concerns in regards to the technology. The time to reclaim a site can be lengthy, particularly if the site is small or has limited amounts of topsoil available in which to incorporate the cuttings. There may also be air quality concerns caused from evaporation of volatile organic compounds from the waste. There is also the possibility of the migration and leaching of soluble salts onto neighbouring land or groundwater.

In a study based more in geochemistry, Chaineau et al. [42] tested the fate and effect of hydrocarbons from oil-based drill cuttings applied via land treatment methods to agricultural fields. Seventy-five percent of the degradation of the hydrocarbon in the waste could be attributed to biotic loss (biodegradation). Chaineau et al. [42] showed that over 90% total reduction in hydrocarbon content of the soil was achieved: the remaining 10% hydrocarbon was composed of proven recalcitrant compounds such as polycyclic aromatics [42]. Additionally, the study investigated the productivity of the soil by planting crops: there was a significant reduction in the crop yield for the fields with the two highest loadings of drilling waste. The difference in crop yield diminished with treatment time [42].

The primary advantages of land treatment include the use of a natural process to treat the oil-based waste and the relatively low cost of the process due to minimal energy input. In terms of cost for the application described in the Amoco Canada Petroleum study [41], employment of land treatment processes was 5 to 7 times less expensive than other commonly used technologies, namely incineration and fixation (inerting). Additionally, if completed at the well site, the waste does not require expensive transport [41, 43]. In comparison to some of the alternative disposal methods, however, land treatment requires a parcel of dedicated land and has a long treatment time [41-43].

2.2.3.2 Alternative Treatment and Disposal Methods of Non-Aqueous Based Drilling Waste

Within *Directive 050*, the ERCB allows for the use of "alternative or innovative disposal methods" for the treatment and safe disposal of hydrocarbon contaminated drilling wastes. Before a technology is permitted for use, the proponent must apply to the appropriate regulatory agency and receive approval [10]. The application for approval must include information on why the alternative method is required, technical details, and potential stakeholder concerns [10].

There are many innovative methods available for the treatment of drilling waste. The methods can generally be divided into three categories: inerting, bioremediation, and thermal treatment [20]. Each category is described with a specific example in the following sections.

Drilling waste reinjection is also considered an alternative disposal method. Since its first use in the 1980s, reinjection has become one of the most widely used disposal methods in the world [33]. Section 2.2.3.2.1 further describes the reinjection disposal method.

2.2.3.2.1 Reinjection

The disposal of drilling waste through reinjection is regulated in Alberta by the ERCB under *Interim Directive 81-01: Subsurface Disposal of Drilling Fluids* [49]. Within *Interim Directive 81-01*, all oil and gas operators within Alberta are permitted to dispose of drilling fluids in any well where it is deemed feasible. Plans for subsurface disposal of drilling fluids must be included in the well drilling program as submitted to the ERCB [49]. Permission to dispose of drilling fluids through reinjection is subject to several conditions including the selection of an appropriate disposal zone (formation), depth of cemented well casing, and well completion plans [33, 49].

The first step in disposal through reinjection involves converting the cuttings from the solids control equipment into a slurry [33, 50]. As shown in Figure 2.4, the cuttings are added to a slurry tank where water is added and the solids are ground [33]. The slurry is then transferred to a holding tank where it is conditioned to achieve the necessary consistency prior to being pumped down the disposal well to the disposal zone [33]. Injection occurs in batches with the disposal well being shut-in after each batch to allow for the dissipation of pressure from the waste within the disposal zone [33, 50].

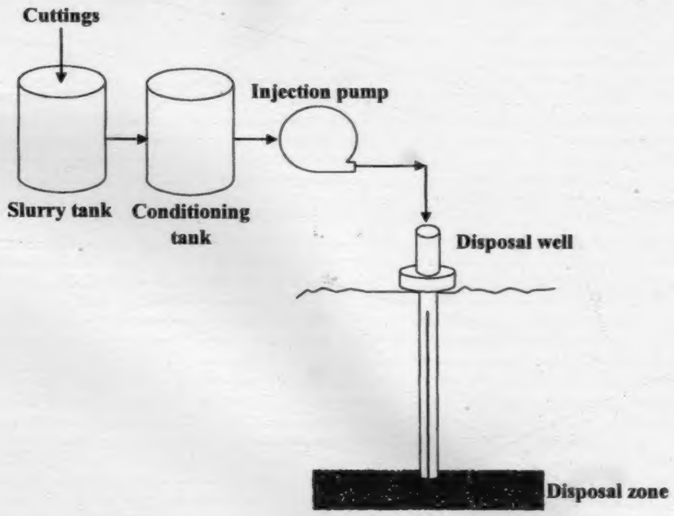


Figure 2.4 Reinjection process diagram, adapted from [33]

Since its first use in the 1980s, reinjection continues to be one of the most widely used disposal technologies [33] due to its many perceived advantages. Reinjection is considered cost-effective and environmentally friendly because it is a zero discharge disposal option and no clean up liability remains after the disposal well is closed [33]. In a cost comparison study published in 1994 [51], reinjection of oil-based drilling waste from North Sea drilling platforms was determined to be the most economical disposal option. The cost of reinjection was compared to the cost of substituting the oil-based drilling fluid with water or synthetic-based fluid (which could be discharged to sea after drilling), as well as to the cost of transporting the oil-based drilling waste to shore for treatment and disposal [51]. The cost of reinjection can be affected by the volume of waste disposed, the possible need for waste transport, and the strictness of the regulations [50]. As such, a site specific cost-benefit analysis is required to determine the least expensive option [50].

2.2.3.2.2 Inerting

Inerting involves fixing the waste so that the harmful substances are not leachable. Interting may be achieved using either solidification or stabilization [50]. Solidification is defined as the encapsulation of waste in a high integrity monolithic solid. The solidification process may be further defined as encapsulation of individual fine waste particles (microencapsulation) or mass encapsulation of the waste in a container (macroencapsulation) [50]. Typically, solidification is a mechanical process whereby the waste constituents are prevented from migrating through either isolation of the waste, or through a reduction in surface area available for leaching [50]. Stabilization, on the other hand, is a chemical process whereby the hazardous components of the waste are converted to a less mobile, less toxic, or less soluble form [50].

In a recent study, a combined solidification/stabilization process was tested on oil-based drill cuttings [52]. The study investigated the use of several binding agents including pure Portland cement and mixtures of Portland cement and blast-furnace slag, microsilica, fly ash, magnesium oxide cement, or hydrated lime [52]. The binders were mixed with the drilling waste at concentrations of 10%, 20%, or 30% and left to cure for 28 days at a set temperature and humidity [52]. After 28 days, leachability tests were performed to determine the effectiveness of the binder in preventing the leaching of oil and chloride [52]. Unconfined strength tests were also completed to determine the suitability of the mixture as a building material [52]. Results of the study showed a decrease in chloride and oil leachability with an increase in binder concentration [52]. Specifically, the 20% and 30% blast furnace slag-Portland cement mixes as well as the 30% lime-Portland cement mix were able to reduce the leaching characteristics of the stabilized solid to below oil and chloride criteria set out for disposal in non-hazardous waste landfills in the United Kingdom. In terms of material strength, the results of the study indicated that the stabilized solid could potentially be used for a variety of construction purposes including burial, blocks, bricks, and ground improvement works [52].

In terms of advantages and limitations, inerting technologies are generally considered of lower cost than some more energy intensive treatments such as thermal desorption (refer to Section 2.2.3.2.4) [50, 52]. Inerting technologies are considerably faster than bioremediation technologies (refer to Section 2.2.3.2.3) [50, 52]; however, the cost may become prohibitive depending on the type and quantity of binder required [50]. Additionally, considerable time and research must be invested into determining the correct type and amount of binder necessary for each drilling waste [50]. Finally, the technology cannot be applied in an offshore setting: the waste must be hauled to shore prior to treatment using inerting technologies [50].

2.2.3.2.3 Bioremediation

Bioremediation technologies employ the use of microorganisms to degrade the hydrocarbons to safe end products: for example water, CO_2, and biomass [43, 50, 53].

The process is optimized by carefully monitoring and controlling the oxygen, water, nutrient, and carbon source (i.e. hydrocarbons) levels within the solid matrix used for the process [43, 50, 53].

The most commonly used bioremediation technologies in the upstream oil and gas industry include land application, composting, and phytoremediation [43, 53]. Land application includes both land farming (also known as land treatment, which is detailed in Section 2.2.3.1) and land spreading [43]. Land spreading involves the one time application of a smaller amount of wastes to a dedicated parcel of land, usually near the site of waste generation [43]. In contrast, land farming involves the application of routinely generated wastes over longer time periods [10, 43, 50]. In Alberta, land spreading is not an acceptable treatment alternative for hydrocarbon contaminated drilling wastes under current regulations [10]; therefore, it will not be further discussed.

Composting involves the incorporation of bulking agents to the waste which increase the aeration and porosity to enhance biological activity [43, 50, 53]. Common bulking agents include wood chips, straw, rice hulls, husks, manure, and peat [43, 50, 53]. Manure and peat have the added bonus of supplying nutrients to the bacteria and fungi responsible for the degradation process [43, 53]. Once the bulking agents are added to the waste, it is placed either in piles or windrows that are aerated by mechanical turning or forced air [43, 50]. Composting requires more attention in implementation than land treatment, but is recommended under the following constraints [43]:

- *When available land space is limited.* Composting generally requires a smaller operational footprint.

- *In cold climates with a growing season less than 4 months*. Composting generates heat that is conserved in the piles, allowing the process to continue in cold weather.
- *In situations of abbreviated treatment time*. Composting can treat large amounts of waste in a relatively short amount of time, which is especially important if regulators have imposed a time constraint on the treatment end point.
- *When the waste hydrocarbon content is high*. Composting has been successfully applied to waste/bulking agent mixes with initial hydrocarbon contents of 15 – 25%.
- *When control of volatile emissions is required*. Compost can be covered or completed in vessels.

The single most important factor in determining the suitability of bioremediation treatment is the composition of the hydrocarbon contaminant [42, 43, 53]. Using combined field and laboratory data from both composting and land application technologies, McMillen et al. [43] at ChevronTexaco developed a rough estimate relating the American Petroleum Institute (API) gravity of the hydrocarbons in the drilling waste to its maximum percent lost through treatment:

$$H = (2.24)(G_{API}) - 19.28, \qquad (3)$$

where H is the maximum hydrocarbons biodegraded measured in percent and G_{API} is the API gravity of the hydrocarbons measured in API degrees (described further in the following paragraph).

API gravity is a measure of the relative density of petroleum liquids, expressed in 'API degrees (°)' [54]. Lighter (i.e. less dense) liquids have higher API gravity [54].

Generally, hydrocarbons with an API gravity >30° are readily biodegraded while those with an API gravity <20° are considered unsuitable for bioremediation techniques [43]. Similar data is presented by Chaineau et al. [53]; heavier lubricating oil is listed at only 30 to 75% biodegradable while gasoline is listed as 100% biodegradable. Petroleum liquids are a complex mixture of saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes [53]. Under optimal conditions, the alkane fraction is first to be degraded in the order of n-, then iso-, then cyclo-alkanes [53]. Aromatics are degraded next, the extent of which decreases with an increase in the number of aromatic rings and atomic substitutions within the rings [53]. The polar fraction of the petroleum liquid, including resins and asphaltenes, is only degraded to a limited extent (less than 20%) [53].

While the relationship described in Equation (3) is used only as a rule of thumb, its development has resulted in no longer needing treatability and pilot studies at many of the ChevronTexaco waste sites [43].

Cost-wise, biological treatment technologies compare favourably to other commonly used treatment techniques [43]. Costs generally decrease as the amount of waste increases [43]. In practice, large scale land treatment can cost anywhere from \$4.40 to \$23.10 per tonne [43]. Composting is slightly more expensive at \$26.40 per tonne [43]. Composting is approximately three to twenty-nine times less expensive than competing thermal technologies and approximately three to twelve times less expensive than currently available solvent extraction techniques [43]. Considering that an average well may produce 1146 m^3 of waste (refer to Section 2.1.4), or 2292 tonnes (assuming a density of approximately 2000 $kg \cdot m^{-3}$ [52]), a savings of a few cents per kilogram becomes a significant factor when determining which treatment method to employ. The main limitations of bioremediation techniques include the treatment duration (months to years) and the increased costs necessary for excavation and transportation in ex-situ applications [53].

2.2.3.2.4 Thermal Treatment

Thermal treatment technologies fall into one of two categories: incineration or desorption [50]. These technologies use high temperatures to either destroy or separate hydrocarbons from the solid matrix of the drilling waste [50]. Thermal treatment techniques may be used alone to achieve a desired total petroleum hydrocarbon end-point or may be used in conjunction with (or as a precursor to) other treatment technologies such as land treatment [50].

While less commonly used than desorption, incineration involves the combustion of drilling waste at very high temperatures (1200 to 1500°C) to convert it to a less bulky and less hazardous material [50]. Incineration of hydrocarbon-based drilling waste is commonly carried out in rotary kilns [50]. The waste enters one end of the kiln and is tumbled in contact with hot exhaust gases from the burner at the opposite end. The burner combusts the hydrocarbons in the drilling waste while the remaining solids, or 'ash', are collected out of the burner end of the kiln for disposal [50].

Thermal desorption uses heat to volatilize hydrocarbons in drilling waste [50, 55]. In a particularly successful application of the technology, a two-stage system consisting of the desorption unit followed by an oil-water separator was employed [55]. In the study, the drilling waste was screened for foreign material and fed by a screw auger into a feed hopper [55]. From the hopper, the material was fed into the desorption unit through a specially designed airlock valve, which controlled the amount of oxygen within the unit [55]. Unlike a rotary kiln used for incineration, the desorption unit was heated in a controlled manner by burners outside the drum [55]: the burner flame did not come into contact with the waste feed material, thereby protecting the hydrocarbons from uneven heating. The temperature of the desorption unit was kept below 220°C to avoid break down of the hydrocarbons [55]. The solids were moved through the drum with screw augers, which also ensured even heating of the solids through conduction with the side of the drum [55]. As the waste was heated, the water and hydrocarbons were driven off as gases [55]. These gases were collected and cooled using direct water sprays prior to entering an oil/water separator [55]. The hydrocarbons were collected for reuse in drilling or as feedstock for the desorption unit burner while the collected water was recycled back to the cooling system [55].

Results of the study are particularly promising. Total petroleum hydrocarbon content and total BTEX (benzene, toluene, ethylbenzene, and xylene) content analyses were conducted on the cleaned solids. A reduction in hydrocarbon content from 340,000 ppm to 230 ppm in the treated solids (>99.9% efficiency) was observed [55]. Similarly, the BTEX content of the treated solids was determined to be <0.48 ppm [55]. The hydrocarbon collected from the process was unchanged in composition as determined from the qualitative analysis by gas chromatography/flame ionization detection [55].

In terms of cost, thermal technologies can be some of the most expensive options for treating hydrocarbon based drilling waste. Incineration costs approximately $330 to $770 per tonne of waste treated [43], while thermal desorption costs approximately $80 to $440 per tonne of waste treated [43, 50, 56]. The increase in cost of thermal treatment technologies over bioremediation technologies is the result of increased energy and labour requirements [56]. The main advantages of thermal techniques include processing speed; a common rotary kiln incinerator installation may treat 0.5 tonnes per hour [50] and the thermal desorption unit used in the aforementioned study has a treatment capacity of 6 to 10 tonnes per hour [55]. Also, in thermal desorption, the collected hydrocarbon can be collected and reused in future drilling operations [50, 55]. A major disadvantage of thermal treatment processes, however, is that they are currently operated as centralized facilities [50], which requires that the waste be transported from its source.

2.3 Supercritical Fluid Extraction

Supercritical fluid extraction (SFE) is one proposed novel technology for the treatment of non-aqueous-based drilling waste. Within the regulatory framework in Alberta, SFE would fit under the 'Alternate Treatment and Disposal' category and therefore would be evaluated and permitted on a case-by-case basis by the ERCB. SFE is categorized as a cleaning technology and would operate in direct competition with existing thermal treatment technologies [20]. The following sections will provide a brief background on the theory of supercritical fluids, a description of common uses of supercritical fluids, and an overview of the research into the use of supercritical fluids as a treatment technology for hydrocarbon based drilling waste.

2.3.1 Properties of Supercritical Fluids

A supercritical fluid (SCF) is a pure substance that exists at or above its thermodynamic critical point, defined by the critical pressure, P_c, and critical temperature, T_c. On a pressure versus temperature curve for a pure substance, the supercritical region can be visualized graphically as the shaded region above and to the right of the critical point, as in Figure 2.5 [57, 58]. The figure shows the interfaces between the three main states of matter (solid, liquid, and gas). The state of the substance is dependant upon the pressure and temperature of the system, assuming a constant volume. At or above the critical point, within the critical region, the substance exists as a merged liquid and vapor.

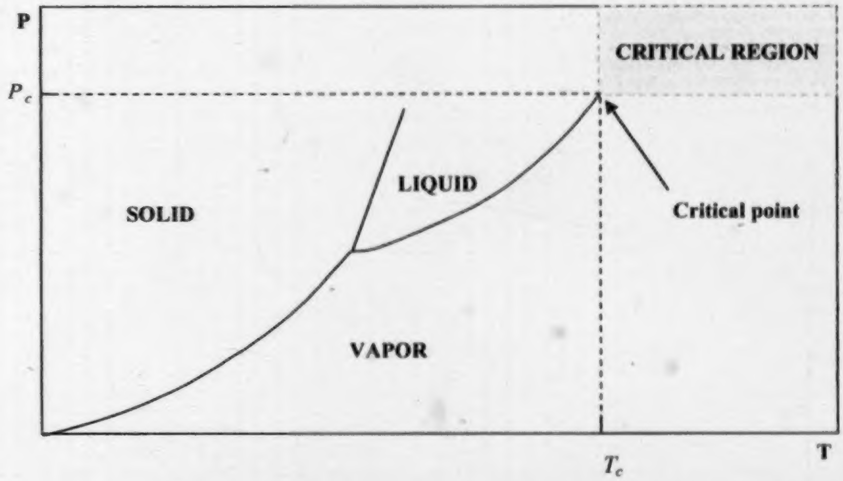


Figure 2.5 General pressure (P) and temperature (T) relationship for a pure substance showing critical point and critical region, adapted from [57, 58]

The properties of the supercritical fluid are intermediate of a liquid and a gas, as highlighted in Table 2.1 [11-14]. Specifically, supercritical fluids have a density similar to liquids but a diffusivity and viscosity similar to vapors: these properties make them particularly attractive for use as solvents in extraction applications. The liquid-like density increases the solvent power of the fluid while the vapor-like diffusivity and viscosity allow the fluid to penetrate solid matrices more easily and, therefore, increases the speed of the extraction [14, 16, 59]. Similarly, supercritical fluids also display a near zero surface tension, which further allows for easier dissolution of the solute from the solid matrix to the SCF [14, 15].

Table 2.1 Typical properties of vapors, supercritical fluids, and liquids [11-13]

State	Density ($g \cdot m^{-3}$)	Diffusivity ($cm^2 \cdot s^{-1}$)	Viscosity ($g \cdot cm^{-1} \cdot s^{-1}$)
Vapor	$(0.6 - 0.2)10^{-3}$	0.1 - 0.4	$(0.6 - 0.2)10^{-4}$
Supercritical Fluid	0.2 – 0.9	$(0.2 - 0.7)10^{-3}$	$(1.0 - 0.9)10^{-4}$
Liquid	0.6 – 1.6	$(0.2 - 2.0)10^{-5}$	$(0.2 - 0.3)10^{-2}$

The state of a pure substance may also be described mathematically. In the realm of fluids, the simplest and most well known of these mathematical relations is the ideal gas law [60]:

$$PV = nRT, \tag{4}$$

where P represents the absolute system pressure; V represents the system volume; n represents the number of moles of the gas; R is the gas constant; and T is the system temperature.

Although simple to apply, the ideal gas law is not well suited for high pressure extractions because it neglects the effects of intermolecular attractions and molecular size. Therefore, for fluid applications, it is generally only used as a tool for estimating variations in state [15].

The two most commonly used equations of state to describe fluids are the van der Waals and the Peng-Robinson. Published in 1873, the van der Waals equation extended the ideal gas law to include terms to describe molecular size and intermolecular attractive forces [15]. The terms in the van der Waals equation, shown below, are as the ideal gas law with v representing the molar volume ($v = V / n$), a representing the attractive forces between molecules, and b representing the molecular volume.

$$P = \frac{RT}{v - b} - \frac{a}{v^2}. \tag{5}$$

While an improvement over the ideal gas law, the van der Waals equation tends to inaccurately describe fluids with liquid-like densities [15]. Additionally, the parameters a and b depend on the critical pressure and critical temperature of the substance, which may not be known with accuracy [15]. An improvement to the van der Waals equation was proposed by Redlich-Kwong in 1949 which allowed for the possibility of knowing the critical points with only limited accuracy [15]. However, the Redlich-Kwong equation introduces a fixed temperature into the attractive term (a). It is postulated by Brunner [15] that attractive forces, such as electrostatic or van der Waals forces, exhibit different temperature dependencies. As it is based on the van der Waals equation, the Redlich-Kwong equation also suffers similar error in the liquid-density range [15].

Perhaps the most widely used expression for describing supercritical fluids is the Peng-Robinson equation, shown below in Equations (6) and (7). Like the Redlich-Kwong, it is based upon the van der Waals equation. It introduces the acentric factor, ω, to better describe molecular structure [15, 57, 59, 61]. The Peng-Robinson equation is [61]:

$$P=\frac{RT}{v-b}-\frac{a\alpha}{v(v+b)+b(v-b)}, \quad (6)$$

with:

$$\alpha^{1/2}=1+\left(0.37464+1.54226\omega-0.26992\omega^2\right)\left(1-\left(\frac{T}{T_c}\right)^{1/2}\right). \quad (7)$$

Despite the fact that the Peng-Robinson equation still suffers from inaccuracies in the liquid density range, it has a considerably higher accuracy, especially in the region surrounding the critical point [15, 61]. For example, it predicts CO_2 properties within 11%, compared to the van der Waals equation that can be in error up to 50% [15].

Many substances are used as supercritical fluids in extraction applications. Some of the more commonly used substances and their critical points are detailed below in Table 2.2.

Table 2.2 Critical conditions of various pure substances [13, 15, 57]

	Critical Temperature (°C)	Critical Pressure (MPa)
Methane	-82.75	4.60
Carbon dioxide	31.0	7.38
Ethane	32.2	4.88
Propane	96.7	4.25
Ammonia	132.5	11.35
Toluene	318.6	4.10
Water	374.2	22.12

Carbon dioxide is the supercritical fluid of choice for many applications. In general, CO_2 is inexpensive, readily available, non-toxic, non-flammable, and has an easily attainable critical point of 31°C and 7.38 MPa [16, 17]. However, SC CO_2 is not a good solvent for polar and ionic compounds because of its inherent non-polarity [62, 63]. To be used as a solvent for the aforementioned applications, the process must be amended with another substance to facilitate dissolution: for example, a methanol co-solvent or a chelating agent [63]. Also, a two-step process with supercritical water may be used in which the supercritical water will extract ionic and polar compounds [62].

The density of supercritical fluids is directly related to the pressure and temperature of the system. As such, the fluids may be 'tuned' in terms of solvent power; one supercritical fluid may replace multiple common liquid solvents in extraction applications [64]. Carbon dioxide is capable, by variation in pressure and temperature, of assuming similar solubility characteristics as many liquid solvents [64] including benzene, toluene, and carbon tetrachloride. These liquid solvents are known for their difficult handling and disposal due to their inherent toxicity to human health and the environment.

2.3.2 Extraction Processes and Applications

A typical supercritical fluid extraction process is shown below in Figure 2.6 [12-14]. In the extraction process, the fluid is heated and pressurized to the desired supercritical conditions and then it is introduced into the extraction vessel. The feed material is also introduced into the extraction step where it is brought into contact with the SCF. Any substances in the feed which are soluble in the SCF will dissolve. The SCF and dissolved compounds proceeds to the separator where, through either a change in pressure or temperature, the extract will precipitate and be collected. The "raffinate" consists of the solids left in the vessel following extraction. Generally, the SCF is recycled to the start of the process. For example, in hydrocarbon contaminated drilling waste treatment, the feed is the drilling waste, the extract is the hydrocarbon, and the raffinate is the cleaned solids.

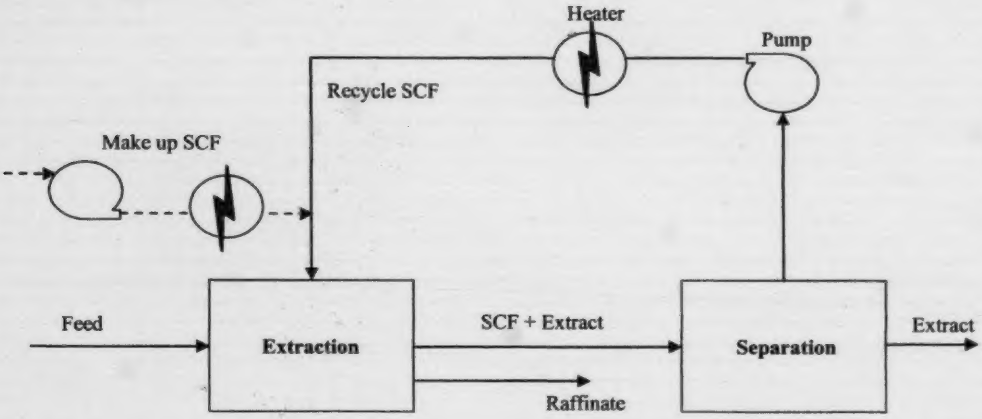


Figure 2.6 **Typical flow scheme of a supercritical fluid extraction process, adapted from [12, 13]**

Extractions may be carried out in one of two ways: batch or counter-current processing [12, 57, 65]. In batch processing, a batch of solid feed material is brought into contact with a continuous stream of SCF. In counter-current processing, both the feed and the SCF are steaming in opposite directions of one another.

The progress of an extraction is unsteady and may be visualized graphically as in Figure 2.7. The initial, positively sloped portion of the curve corresponds to a constant rate of extraction. This constant rate of extraction has been hypothetically attributed to either equilibrium between the SCF and the soluble extract or a constant resistance to mass transfer or some combination of the two [12]. In the latter part of the curve, the extract yield begins to flatten out and approach a limiting value, indicating that the maximum amount of extract has been recovered from the feed material [12].

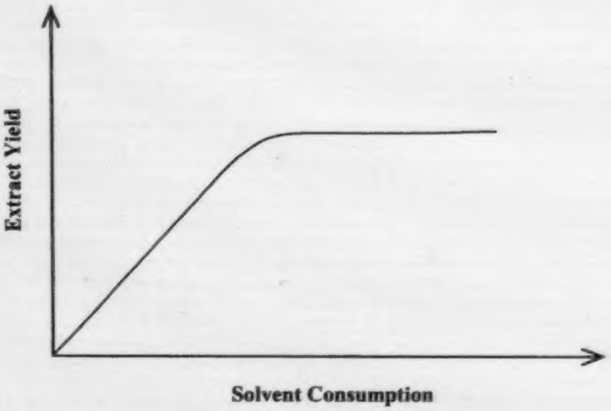


Figure 2.7 **Typical extraction progress curve, adapted from [12, 15]**

Extraction with SCFs has already been applied successfully at a commercial scale, most notably in the food industry for the decaffeination of coffee and tea, the extraction of bitters from hops, and the extraction of essential oils and flavours [12, 57]. In terms of size, the pressure vessels used for these applications range in size from 1 to 40 m^3 [57]. Decaffeination facilities are generally the largest installations of SFE with vessels 20 m^3 and larger [57]. Most food applications of SFE involve the use of CO_2 because it does not leave a harmful residue on the raffinate (for example, the decaffeinated coffee beans or tea leaves) [16, 17]. The first decaffeination facility for coffee was built in Germany in 1978 by the Hag AG Corporation: it processes 50 million kilograms per year [64]. Shortly following that, a 7 million kilograms per year tea decaffeination facility was built by SKW/Trosstberg, also in Germany [57, 64]. The extraction vessels in that particular facility are two stories tall and approximately 2 m in diameter; in one extraction cycle, each vessel is fed 910 kg of tea leaves [57].

2.3.2.1 Treatment of Hydrocarbon Contaminated Soils Using Supercritical Fluid Extraction

Closely related to the topic of this research, SFE using SC CO_2 has also been successfully applied in the removal of petroleum hydrocarbons from contaminated soils. Extraction conditions for these studies are shown below in Table 2.3.

Table 2.3 Summary of studies completed using SC CO_2 to treat hydrocarbon contaminated soils, adapted from [66]

Ref	Soil	Hydrocarbon	Extraction Conditions	
			P (MPa)	T (°C)
[67]	Spiked sand	Diesel	10.1 – 15.2	40 – 80
[68]	Field-contaminated soil*	Fuel	20.3	77 – 80
[69]	Spiked loam	Diesel	12.9	60
[70]	Spiked sandy clay loam	Saturated & aromatic fractions of crude oil	23.0	80
[71]	Spiked sandy clay loam, clay loam, sand, clay & loamy sand	Diesel	30.4	50
[72]	Field-contaminated top soil	Diesel	37	80
[73]	Field-contaminated soil*	Diesel and gasoline	34.5	80
[74]	Field-contaminated clay loam, Spiked loamy sand	Weathered petroleum hydrocarbons/Diesel	20	50 – 100
[75]	Field-contaminated soil*	Petroleum hydrocarbons	25.3 – 40	80 – 150
[76]	Field-contaminated soil*	Diesel and gasoline	34.5	80
[77]	Field-contaminated loam, sand, loamy sand, sandy loam & silt loam	PAHs	7.7 – 34	40 – 120
[78]	Spiked sandy loam & marine sediment	PAHs	23 – 60	50 – 80
[79]	Field-contaminated soil*	PAHs	40	90
[80]	Spiked sand & sandy clay	Pyrene	7.5 – 25	40 – 60
[81]	Field-contaminated soil*	Petroleum hydrocarbons, PAHs	10.1	50 – 150
[82]	Field-contaminated soil* mixed with spiked soil	Petroleum hydrocarbons, PAHs	35 – 35.5	100 – 150
[83]	Field-contaminated soil*	PAHs	12 – 40	50 – 150
[84]	Field-contaminated clay loam & sandy clay loam	PAHs	11 – 14	50
[85]	Field-contaminated soil*	PAHs	10 – 40	90
[86]	Spiked diatomaceous earth	Diesel fuel	20.3 – 50.7	50 – 70
[17]	Field-contaminated clay loam & sandy clay loam	PAHs	10.1	34.9 – 54.9
[87]	Spiked topsoil	PAHs	55	6.9 – 13.8
[88]	Field-contaminated sand, silt & clay	PAHs	7.6 – 27.3	33 – 77
[89]	Field-contaminated soil*	PAHs	20 – 40	90
[90]	Field-contaminated soil*	PAHs	20	90 – 120
[91]	Field-contaminated sediment	PAHs	7.6 – 32.9	50 – 150
[92]	Soil-water slurry*	PAHs	10.1 – 22.1	35 – 45
[93]	Spike silt and field-contaminated soil*	PAHs	30	80 – 130
[94]	Spiked and field-contaminated marine sediments and road bed soil	PAHs	10.7 – 65.9	40 – 200
[95]	Field-contaminated soils*	PAHs	40.5	50 – 350

* – soil type not specified in study

As can been seen in Table 2.3, SFE with SC CO_2 has been tested under a variety of conditions. However, despite the large range in test conditions, the effectiveness of the extraction is largely dependent on a few main factors, namely modifier use, fluid density, and water content [14, 66, 96]. Modifiers are organic solvents, such as methanol, that are added soil matrix to allow the solute to be more easily removed by the SCF [14, 66, 96]. Modifiers increase the solubility by enhancing the polarity of the SCF [14, 66, 96]; by displacing contaminants from active sites in the soil and preventing their readsorption [66]; and by causing clay soil types to swell, thereby allowing contaminants to move more freely from interstitial pores [66].

Fluid density, defined by operating pressure and temperature, is one of the most important factors affecting the solubility of contaminants in SFE [66, 96]. Particularly, an increase in pressure generally results in an increase in extraction efficiency by increasing the fluid density [66, 96]. Temperature has two important and opposing effects: increasing the temperature increases the volatility of the hydrocarbon but it also decreases the density of the fluid [66, 96].

Water content can increase or decrease extraction efficiency through its influence on the binding of hydrocarbons to the soil [66, 96]. While further investigation is required, it has been hypothesized that water interacts with clay particles in soil. As with modifiers described above, this causes the clay to swell, therefore increasing the mobility of trapped hydrocarbons [66, 96]. Water may also bind to active sites in soils, preventing hydrocarbons from bonding to them [14, 66, 96]. Water, however, may also reduce extraction efficiency by limiting contact between the SCF and the hydrocarbon as well as inhibiting hydrocarbon volatility [66].

2.3.2.2 Extraction of Hydrocarbons from Drilling Waste

While the amount of research documenting the use of SFE for remediation of hydrocarbon contamination from soils is quite vast, the use of SFE specifically for the removal of hydrocarbons from drilling waste is a fairly underdeveloped field. Table 2.4 highlights the major points of the studies that have been completed to date.

Table 2.4 Summary of studies completed using super- or near-critical fluid extraction to treat hydrocarbon-contaminated drilling waste

Reference	Waste Samples	Contaminant Hydrocarbons	Sample Size (g)	Fluid	Extraction Pressure (MPa)	Extraction Temperature (°C)
[18]	Cuttings[1] Fines[2]	Diesel, Asphalt, No. 4 fuel oil	10 – 300	CO_2	9.7 – 22.1	30 – 70
				Freon	3.4 – 8.3	60
				Propane	3.4 – 8.3	45 – 65
[19]	Cuttings	Oil-based[3]	251 – 279	Propane	5.2 – 7.6	104
				Freon	5.2	121
[20]	Cuttings	Oil-based	200 – 6000	CO_2	6 – 12	35 – 45
[22]	Fines	Diesel	10	CO_2	8.3 – 17.2	35 – 60
[23, 24]	Cuttings	Oil-based	1	CO_2	6.9 – 24.1	ambient – 43
[21]	Fines	Diesel	100	CO_2	8.9 – 15.2	40 – 60
[25]	Cuttings	Diesel, Mineral oil, Synthetic	Not stated	Butane	3.4	ambient
				Propane	3.4	ambient
[26]	Cuttings	Oil-based	Not stated	CO_2	6.8	20

[1] *Cuttings* – larger grain size such as rock chips, typically obtained from shale shakers and hydrocyclones
[2] *Fines* – smaller grain size such as clay, typically obtained from centrifuge underflow
[3] *Oil-based* – specific hydrocarbon not specified

The first study, a patent by Eppig et al. [18] in 1984, investigated the use of supercritical propane, Freon, and CO_2 for the treatment of a variety of drilling wastes. No quantitative results were given for the hydrocarbon content of the solids after extraction, though visual observations such as, "dry, non-oily, free flowing" indicated a positive result [18].

In 1996, Eldridge [19] published the results of a study that investigated a pilot scale SFE system for the removal of hydrocarbons from drilling waste on North Sea oil platforms. The system achieved 98% removal of hydrocarbons using supercritical propane and Freon. The study also determined that the use of SFE for treatment of drilling waste offshore was more economically feasible compared with other options including a 20 well reinjection program, onshore processing, and substitution of the oil-based drilling mud with water or synthetic-based muds [19, 51].

Saintpere and Morillon-Jeanmaire [20] investigated the treatment of oil-contaminated drill cuttings from offshore in the North Sea using SC CO_2. The first phase of the study was completed at a bench-scale with the extraction system being able to handle 200 g of cuttings [20]. Using process conditions of 10 MPa and 35°C, the hydrocarbon content on the solids after extraction was 1% [20]. The second phase of the study investigated the use of a larger extraction system, capable of handling up to 6 kg of waste and again, residual hydrocarbon contents at or below 1% were observed [20]. Comparing the chromatograms of the hydrocarbon before and after extraction indicated that the hydrocarbon constituents were unaltered by the process [20]. Recognizing the importance of good SCF-waste contact, a third phase, which incorporated agitation, was attempted. However, the larger system that was tested (up to 10 kg of waste) suffered severe downstream clogging caused by fine particles entrained in the fluid flow as a result of the agitation [20]. No results were reported for the third phase of the research program.

The first of two SFE studies for drilling waste treatment undertaken in the Department of Civil and Environmental Engineering at the University of Alberta was completed in 2003 by Odusanya [22]. The research investigated the extraction of diesel from centrifuge underflow drilling waste using SC CO_2 [22]. Through alterations in process temperature and pressure, the hydrocarbon content of the waste was reduced from 17% to 0.6% at 12.4 MPa and 50°C [22]. Similar to the study by Saintpere and Morillon-Jeanmaire, the study also concluded that the hydrocarbon was not altered in composition by the extraction process, leading to the potential for reuse [22]. The study recommended mixing to improve contact between the SC CO_2 and the waste [22].

The second study from the University of Alberta, completed in 2004 by Lopez Gomez [21], built upon the results and recommendations of the first. A mixer was introduced to the reaction vessel, and the process was optimized in terms of pressure, temperature and mixing speed [21]. The optimum process parameters were determined to be 14.5 MPa, 40°C, and 800 rpm, resulting in a reduction in hydrocarbon content from 19.4% to 0.3% [21]. The study confirmed, through visual observation of chromatography results, that the hydrocarbon was not altered by the extraction process [21].

Patent applications by Tunnicliffe and Mt. Joy in 2002 and 2004 [23, 24] described a bench-scale system for the removal of hydrocarbons from drill cuttings using near supercritical CO_2. The system consisted of an 8 mL, stainless steel, in-pipe extraction vessel that held 1 g of contaminated drill cuttings [23, 24]. No quantitative results were given in the patent applications, but qualitative observations of the treated solids indicated an optimum process condition of 24.1 MPa at ambient temperature [23, 24].

In 2005, Seaton and Hall [25] tested near supercritical propane and butane extraction as a treatment for diesel, mineral oil and synthetic contaminated drill cuttings.

Acknowledging the potential safety risk in using propane and butane as SCFs, the tests were performed at ambient temperature [25]. The obvious advantage to using these fluids is the lower pressure required [25]. The initial test set up showed good results, with the lowest observed residual oil content reported at 0.5% [25]. However, uneven flow or 'channeling' of the SCF through the drilling waste mass was observed, highlighting the necessity for mixing [25]. The second set of tests incorporated ceramic pellets and a "jar rolling mill" to encourage even distribution of the SCF through the waste and improve mass transfer of the hydrocarbon to the fluid [25]. The results for the second set of tests had reported residual hydrocarbon contents from 'trace' to 0.53% [25]. As with previous studies, Seaton and Hall [25] confirmed that the hydrocarbon is unaltered in the extraction process.

In a 2006 patent, Massetti et al. [26] describe a system for the "removal and recovery of the oily component from drill cutting with liquid CO_2". Although experimental results given in the patent are limited, the system was able to achieve 1.0% final hydrocarbon content on the treated cuttings using liquid CO_2 at 6.8 MPa and 20°C [26].

The results of the research studies and patents described in Section 2.3.2.2 were obtained through a change in supercritical fluid density on a given extraction system design. While all the studies report favourable extraction results, some also report process problems such as fluid channeling and solids carryover. None of the studies detail solutions to these process issues. The objectives of this research is to take previously determined optimum conditions in terms of fluid density and instead alter parameters such as mixing, waste quantity, waste character, and vessel design in order to solve process issues.

CHAPTER 3 - MATERIALS AND METHODS

The following sections will highlight the materials and methods used in this research. Chapter 3 will discuss the supercritical fluid extraction system and the Soxhlet extraction/gas chromatography used to determine the extraction efficiency of the SFE process.

3.1 Experimental Materials

Section 3.1 will discuss the materials used for the SFE process and for the quantification of the results. Specifically, the following will be discussed:

- the drill cuttings;
- the chemicals including solvents, standards, and waste additives; and
- the supercritical fluid extraction system.

3.1.1 Drill Cuttings

The centrifuge underflow drill cuttings used in the extraction were provided by M-I SWACO (Calgary, Alberta, Canada) from an active drill site in the same geographical region. The cuttings were placed in 4°C cold storage at the Department of Civil and Environmental Engineering at the University of Alberta until they were used in the extraction.

The cuttings were contaminated with the base oil HT 40 N, formulated by Petro-Canada Lubricants (Mississauga, Ontario, Canada). The base oil is an enhanced mineral oil produced from Petro-Canada's "HT Purity Process", which involves severe hydrocracking, or breaking up of heavy molecules into lighter ones [97]. The "HT Purity

Process" is undertaken at conditions of 400°C and 2.1 MPa in the presence of a catalyst [97]. As a result, impurities such as polar compounds containing nitrogen, sulphur, and oxygen are removed [97]. The process also breaks aromatic hydrocarbons into saturated cyclic hydrocarbons [97]. The "HT Purity Process" produces base oils with numerous benefits, most notably their biodegradability: 60% in comparison to 30% for traditional solvent refined oils [97]. The final base oil product is clear, colourless, odourless, and has a density of 0.85 $kg \cdot L^{-1}$ at 15°C [98, 99].

The cuttings themselves had an initial hydrocarbon content of 12.7 ± 1.4% (further details on how the initial hydrocarbon content was determined are given in Section 4.2.2). The cuttings were dark brown in colour with a fudge-like texture. A photo of the cuttings is shown below in Figure 3.1.

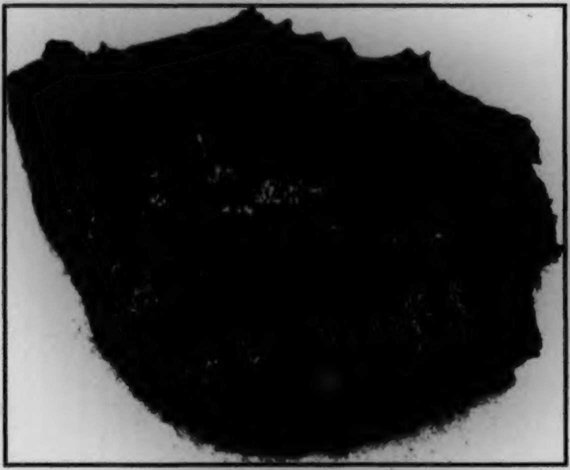


Figure 3.1 Photo of drilling waste used in this research, approximate scale 2:1

3.1.2 Chemicals and Laboratory Consumables

The following table lists the chemicals and laboratory chemicals used within this research, pertinent quality details, and the supplier.

Table 3.1 List of chemicals and other materials used in this research

Chemical	Use	Supplier
Carbon Dioxide, grade 3 (bone dry)	Supercritical solvent	Praxair (Mississauga, Ontario, Canada)
Hexane, HPLC grade	Soxhlet extraction	Fisher Scientific (Ottawa, Ontario, Canada)
Acetone, HPLC grade	Soxhlet extraction	Fisher Scientific (Ottawa, Ontario, Canada)
Toluene, HPLC grade	Soxhlet extraction, GC/FID standards	Fisher Scientific (Ottawa, Ontario, Canada)
Decane ($C_{10}H_{22}$), 99%	GC/FID standards	Acros Organics (Geel, Belgium)
Hexadecane ($C_{16}H_{34}$), 99%	GC/FID standards	Acros Organics (Geel, Belgium)
Tetratriacontane ($C_{34}H_{70}$), 98%	GC/FID standards	Sigma-Aldrich (St. Louis, Missouri, USA)
Pentacontane ($C_{50}H_{102}$), ≥97%	GC/FID standards	Sigma-Aldrich (St. Louis, Missouri, USA)
Diesel fuel	GC/FID standards	Commercially available (Edmonton, Alberta, Canada)
Motor oil, Motomaster Nugold 5W30	GC/FID standards	Canadian Tire (Toronto, Ontario, Canada)
Sodium sulfate, 10-60 mesh	Soxhlet extraction	Fisher Scientific (Ottawa, Ontario, Canada)

3.1.3 Supercritical Fluid Extraction System Setup

The extraction vessel used in this research is a bolted closure reactor (Autoclave Engineers, Erie, Pennsylvania, USA) [100]; refer to Figure 3.2.

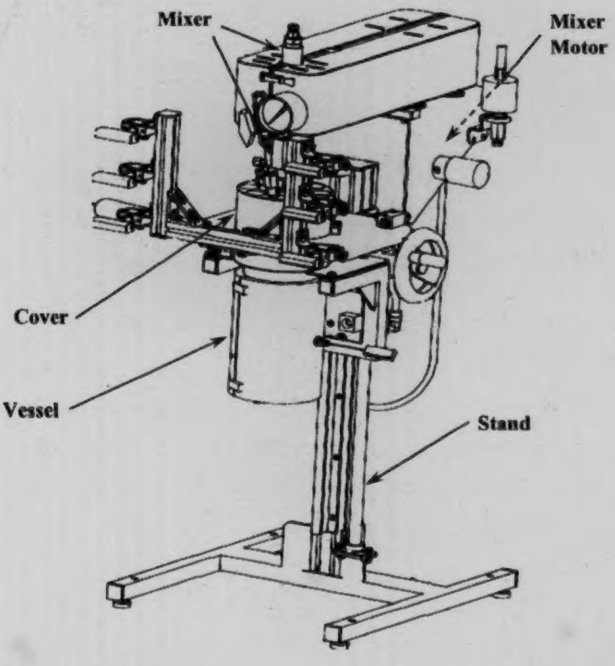


Figure 3.2 **Supercritical fluid extraction system, approximate scale 1:10, adapted from [100]**

The vessel, made of 316 stainless steel, has an internal volume of 300 mL and is rated with a maximum allowable working pressure of 37.9 MPa at 343°C [100]. The vessel is surrounded by a heating jacket through which hot water is circulated to attain the desired temperature of the extraction.

The extraction system is also equipped to accommodate mixing. A ribbon blender (Figure 3.3) with two sets of helical blades (PRECIMAX, Edmonton, Alberta, Canada) is mounted to the drive shaft of a MagneDrive® mixer (Autoclave Engineers, Erie, Pennsylvania, USA). Mixing power is supplied through a belt by a 0.37 kW (1/2HP), 120 V DC motor. The MagneDrive® mixer is rated to a maximum speed of 3300 rpm, supplying a maximum torque of 0.79 N·m. The speed of the motor is controlled electronically and monitored with magnetic sensors within the MagneDrive®.

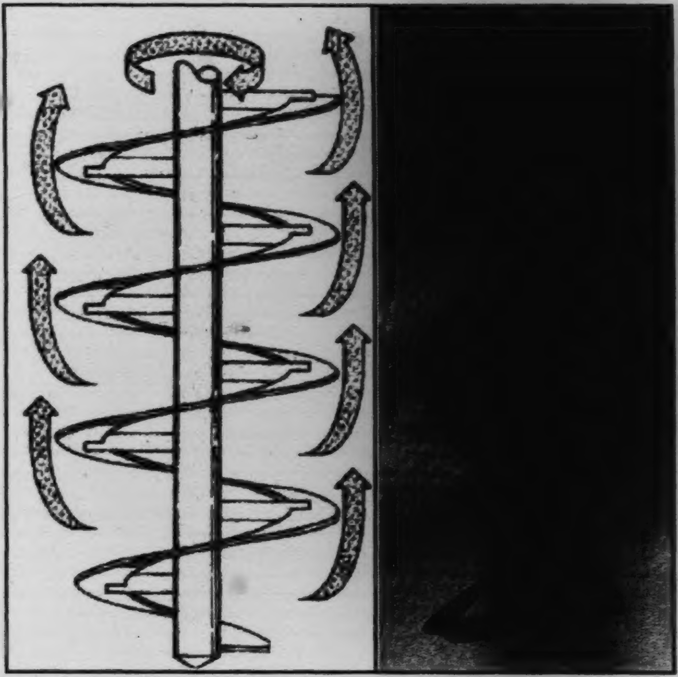


Figure 3.3 **Ribbon blender, showing mixing action (left) adapted from [101]; and photograph of actual lab installation (right), approximate scale 1:1**

The reactor vessel cover (Figure 3.4), also stainless steel, is fixed to the stand thereby enabling the vessel to be removed without interfering with the inlet, outlet, and pressure relief connections. In the particular set up used for this research, only the inlet, outlet, and safety vent were in use; the rest of the connections indicated in the figure were closed.

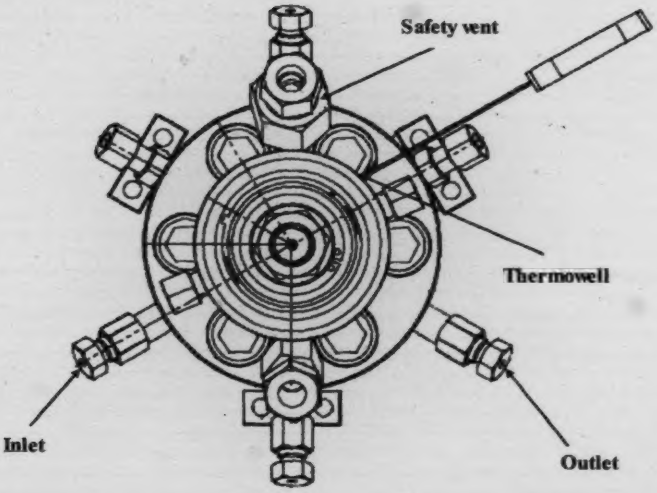

Safety vent
Thermowell
Inlet
Outlet

Figure 3.4 Extraction vessel cover, top view, approximate scale 1:3, adapted from [100]

The following photograph and schematic diagram (Figure 3.5 and Figure 3.6, respectively) show the full laboratory setup of the SFE system.

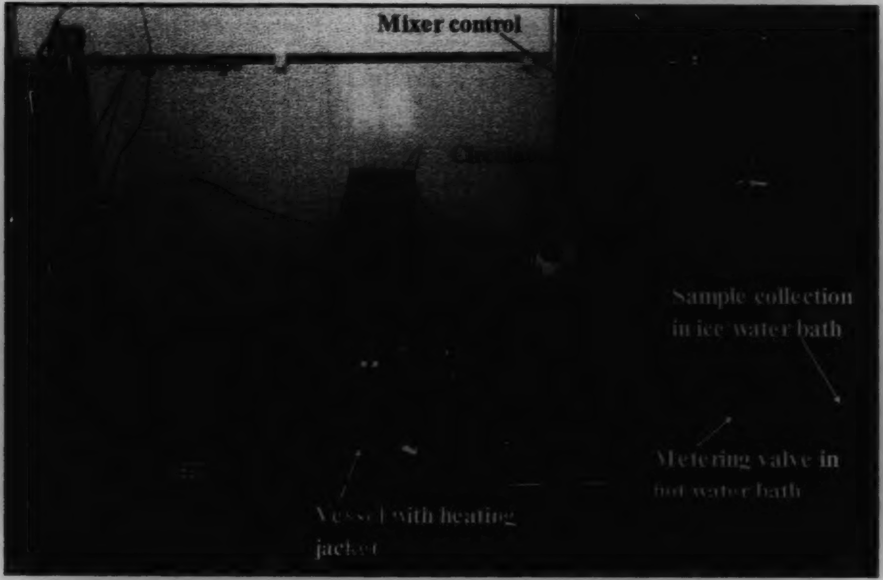
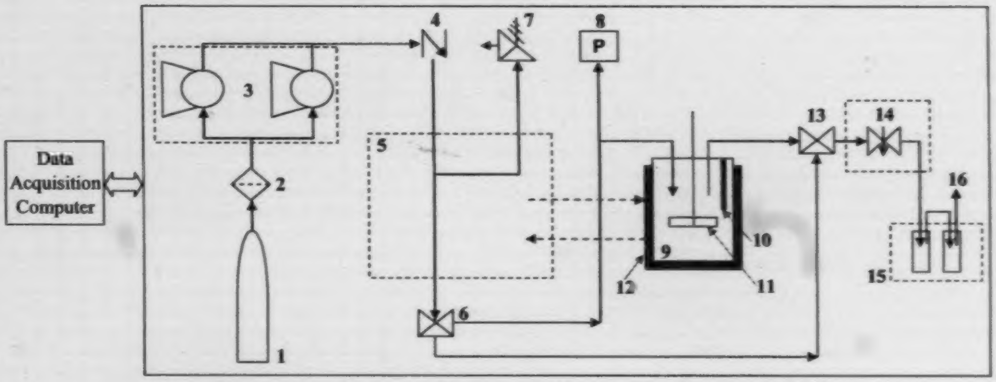

Mixer control
Sample collection in ice water bath
Metering valve in hot water bath
Vessel with heating jacket

Figure 3.5 Photo of laboratory SFE setup



Legend:

1. Carbon dioxide feed cylinder
2. Filter
3. Syringe pumps, circulating water cooling system
4. Check valve
5. Hot water bath
6. 3-way valve
7. Pressure relief valve
8. Pressure transducer
9. Extraction vessel
10. Thermistor probe
11. Ribbon blender
12. Heating jacket
13. 3-way valve
14. Metering valve, hot water bath
15. Sample and vent vials, ice water bath
16. Carbon dioxide vent to fume hood

Figure 3.6 Schematic showing the main components of the SFE system used in this research, adapted from [21]

Following Figure 3.6, liquid CO_2 is fed from the cylinder (1) at approximately 5 MPa (depending on the fill level in the tank). It passes through a 0.5-micron filter (2) into two, ISCO 500D syringe pumps (Teledyne ISCO, Lincoln, Nebraska, USA) operated in parallel and cooled to 7.5°C by a circulating refrigerated water system (3). The pumps pressurize the CO_2 to the desired pressure (14.5 MPa in this case). The pressurized fluid then flows through a check valve (4) which prevents flow from reversing back to the pumps and potentially damaging them. The flow passes through a heated, circulating water bath (5) where it is warmed to the desired temperature (40°C in this case). Although not indicated in the figure, the tubing which passes through the water bath is coiled to allow sufficient time for the CO_2 to be warmed. The hot water in the water bath is also circulated to and from the heating jacket (12) on the extraction vessel (9). There is also a pressure relief valve (7) on this line, which is set at 17.24 MPa. The relief valve ensures that the system pressure does not exceed safe operating limits.

The CO_2, now at supercritical conditions, flows through a 3-way valve (6) to the extraction vessel (9). From the valve, the flow may also bypass the extraction vessel to a second 3-way valve (13) and the outlet. This provides a mechanism for purging the outlet lines with clean CO_2 if needed.

The pressure and temperature in the extraction vessel are monitored using a pressure transducer on the inlet line (8) and thermistor probe within the vessel (10). The extraction vessel is also equipped with a ribbon blender for mixing (11).

The SC CO_2 leaves the vessel, passing through the vessel outlet, through a 3-way valve (13) to the metering valve (14). The metering valve controls the fluid flow rate through the system. After the metering valve, the fluid expands to atmospheric pressure. This expansion can cause the outlet lines to freeze, so a second hot water bath is used for the valve and nearby lines. The gaseous CO_2 then flows to through the sample and vent vials contained in an ice water bath (15). The vent vial collects any hydrocarbon that is carried over from the sample vial in the CO_2 flow. The CO_2 is then vented to the laboratory fume hood (16).

Operational data from the pumps, pressure transducer, and thermistor probe are collected every 10 seconds throughout an extraction using the data acquisition software. Further information on data acquisition is provided in Section 3.2.1.

3.2 Methods

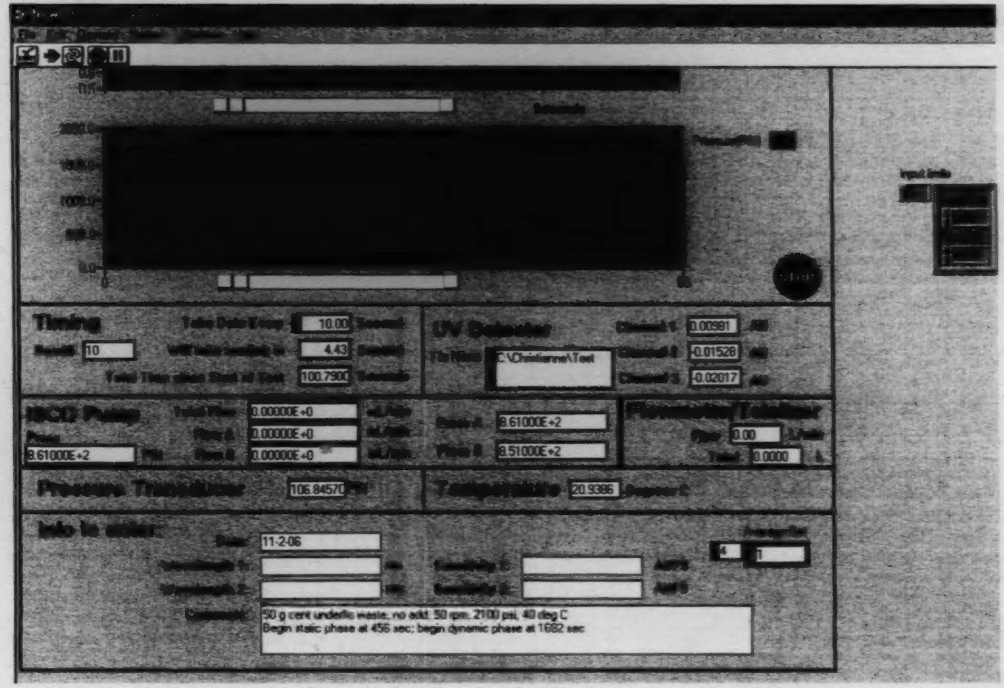
The following sections detail the procedures used in the supercritical fluid extraction as well as the subsequent hydrocarbon analysis used to determine the efficiency of the extraction process.

3.2.1 Supercritical Fluid Extraction Procedure

As previously indicated in the study objectives, the optimum extraction conditions of pressure and temperature of 14.5 MPa and 40°C were determined in a previous study completed at the University of Alberta [21]. The SFE procedure used in this research is detailed in the following steps:

1. A predetermined mass of drill cuttings was placed in the cleaned reactor vessel. In this research, extractions were completed using 50 g, 100 g, and 150 g of drill cuttings. The drill cuttings were weighed using the laboratory balance (Mettler-Toledo International Inc., Columbus, Ohio, USA). If additives were used, they were added and mixed by hand. The mass of additive used was determined using the same laboratory balance.
2. The vessel outlet line was plugged with silane treated glass wool and glass filter circles to prevent entrainment and carryover of solid particles, which may clog the downstream lines and valves.
3. The vessel was bolted into place using a torque wrench and a specific bolt tightening sequence of 33.9, 47.5, and then 56.9 N·m. By tightening in stages to the maximum torque, leaks are prevented.

4. The water bath was filled with water and connected to the heating jacket of the vessel via plastic tubing. A heating circulator pumped the water through the tubing and the jacket and also maintained a steady vessel temperature. A standard glass thermometer was also used to monitor and verify the temperature of the water bath.
5. LabView 5.1 data acquisition software (National Instruments, Austin, Texas, USA) was initiated to monitor the pressure, temperature, and flow rate of CO_2 from the pumps. A sample of the LabView 5.1 control screen is shown in Figure 3.7. Data is acquired every 10 seconds during an extraction; this includes time (s); both combined and individual pump flow rates ($mL \cdot min^{-1}$); individual pump pressure (psi); vessel temperature (°C); and vessel pressure (psi). The data is used largely to monitor these parameters during the extraction; however, the data may be imported in to MS Excel for further analysis.



Timing

10

10.00 Seconds

4.43 Seconds

Total Time since Start of Test 100.7900 Seconds

UV Detector

File Name C:\Christianne\Test

Channel 1 0.00981

Channel 2 -0.01528

Channel 3 -0.02017

ISCO Pump

8.61000E+2

0.00000E+0

0.00000E+0

0.00000E+0

8.61000E+2

8.51000E+2

Flowmeter/Totalizer

Flow 0.00

Total 0.0000

Pressure Transducer 106.84570

Temperature 20.9386

Info to enter:

Date 11-2-06

4

1

Comments 50 g cent underflo waste; no add. 50 rpm. 2100 psi, 40 deg C
Begin static phase at 456 sec; begin dynamic phase at 1682 sec

Figure 3.7 LabView data acquisition software control screen

6. The syringe pumps were filled and pressurized to the extraction pressure of 14.5 MPa.
7. The mixer was started and set to the desired speed using the electronic control. In these experiments, 50 and 100 rpm were tested.
8. Once the vessel reached the desired extraction temperature of 40°C, the valve from the pumps to the vessel was opened and the vessel was pressurized to 14.5 MPa.
9. Once the vessel was fully pressurized and the readings for pressure, temperature, and flow rate stabilized, a 15 minute static period began. All times were monitored using a stopwatch.
10. During the static period, seven sample vials were prepared and weighed. Each consisted of a glass 40 mL environmental sample vial approximately 1/3 filled with

glass beads and topped with silane treated glass wool. The screw threads on the sample vials were Teflon®-taped to ensure a tight seal on the SFE system outlet port. The first sample collection vial and the overflow, or 'vent vial', were attached to the outlet port. The sample vials were placed in an ice water bath to inhibit possible volatilization of hydrocarbons.

11. Once the static period was completed, the 90 minute dynamic period began. The outlet valves were opened and adjusted to set the desired CO_2 flow rate from the pumps (9.6 to 19.3 $g{\cdot}min^{-1}$ and 28.9 to 38.5 $g{\cdot}min^{-1}$ were tested in these experiments). The vent vial remained in place for the entire extraction, while the other sample vials were replaced every 15 minutes during the dynamic phase. After removal from the system, the vials were left to de-ice and de-gas prior to determining their final mass.
12. Once the 90 minute dynamic period completed, the pump valve was turned off and the vessel was allowed to depressurize. After depressurization, the outlet lines were purged to clean out any remaining hydrocarbons. Purging was accomplished using CO_2 directly from the pumps, which bypassed the vessel. During depressurization and bypass, the last sample vial and vent vial remained in place on the outlet port to collect any hydrocarbons that may have been deposited in the outlet lines.
13. The pumps were then turned off and the pump valve was closed. All other lines were depressurized and the vessel was removed from the system. The cleaned cuttings were collected from the vessel in glass environmental sample jars for further analysis. The hydrocarbon content of the solids before and after extraction were determined using the *Reference Method for the Canada-Wide Standard for*

Petroleum Hydrocarbons in Soil – Tier 1 Method from the Canadian Council of Ministers of the Environment (CCME) [102] described in Section 3.2.2.

3.2.2 Procedure for Determining Total Petroleum Hydrocarbon Content

The CCME *Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil – Tier 1 Method* [102] was used in this study to determine the total petroleum hydrocarbon content of the drilling waste samples before and after treatment with SFE. The CCME procedure was published in 2001 to harmonize and standardize petroleum hydrocarbon analysis from laboratories across Canada and allow for comparability of results.

The procedure determines the total petroleum hydrocarbon content of a sample in four fractions or hydrocarbon ranges. These are F1 (nC6 to nC10), F2 (nC10 to nC16), F3 (nC16 to nC34), and F4 (nC34 to nC50). The method recommends that both BTEX (benzene, toluene, ethylene, and xylene) and PAHs be reported separately from the total petroleum hydrocarbon result. However, testing for BTEX and PAHs is only required if their presence is reasonably suspected in the sample. The method does not provide for the determination of individual hydrocarbons, nor has it been tested on all hydrocarbon/soil combinations. However, it is applicable to most soil and sediment samples from sites contaminated with refined hydrocarbons [102].

In this research, analysis was completed for the F2, F3, and F4 range of hydrocarbons. The F1 fraction was not considered since the lighter, and therefore more volatile hydrocarbons, would be volatilized during the mechanical processing of the drill cuttings.

The following sections detail the application of the CCME method in determining the hydrocarbon content drill cuttings before and after treatment with SFE and the method for calculating the extraction efficiency. Also included are details on the calibration of the gas chromatograph for the CCME method and the quality control procedures used.

3.2.2.1 Gas Chromatography Calibration

The CCME method requires a gas chromatography system equipped with a flame ionization detector (GC/FID) and a 100-percent poly(dimethylsiloxane), low bleed chromatography column with a length of at least 15 m. The inner diameter of the column must not exceed 0.53 mm [102].

The GC/FID used for petroleum hydrocarbon sample analysis in this research is a Varian CP-3800 (Varian Inc., Palo Alto, California, USA) equipped with a CP-8410 AutoInjector system. The autoinjector system has a capacity for ten 2 mL sample vials, six 5 mL sample vials, and five 10 mL sample vials. In this investigation, the 2 mL sample vials were used for samples and three of the five 10 mL sample vials were used for clean solvent and syringe rinse waste. The GC/FID also had a Varian CP-1177 split/splitless injector. The following table details the GC/FID setup used in this research.

Table 3.2 Gas chromatogram setup for petroleum hydrocarbon analysis

Parameter	Details
Hydrogen column flow rate	• 18 $\mathrm{mL\cdot min^{-1}}$
Hydrogen makeup flow rate	• 12 $\mathrm{mL\cdot min^{-1}}$
Detector air flow	• 487 $\mathrm{mL\cdot min^{-1}}$
Detector hydrogen flow	• 11 $\mathrm{mL\cdot min^{-1}}$
Injector temperature	• 280°C
Injection volume	• 2 µL
Split/splitless program	• Begin with spilt on (split ratio of 10), at 0.01 seconds split is turned off, at 0.75 seconds split is turned on (split ratio of 50), at 2 minutes split ratio is 10
Column temperature program	• Begin at 40°C, hold for 2 minutes, at 2 minutes increase to 320°C at 20°C per min, hold for 8 minutes
Column	• Restek (Fisher Scientific, Ottawa, Ontario, Canada), 100% dimethyl polysiloxane, Length: 30 m, Inner diameter: 0.32 mm, Maximum programmable temperature: 350°C, Minimum bleed temperature: 330°C

For analysis in the F2 to F4 range (nC10 to nC50), the following items are required for GC/FID calibration under the CCME method [102]:

- The primary calibration standard must be a mixture of approximately equal parts of nC10, nC16, and nC34 hydrocarbons prepared in toluene. A minimum 3-point calibration curve must be generated using this standard. Keep in mind that any sample peaks must lie between the highest and lowest standard peaks.
- A nC50 standard must also be prepared in toluene to a maximum concentration of 15 mg·L-1 (due to its low solubility).
- The nC50 response factor must be within 30% of the average nC10, nC16, and nC34 response factor.
- The individual nC10, nC16 and nC34 response factors must be within 10% of each other. This must be checked on a daily basis using the low and mid-point

concentrations in the calibration curve. These must not deviate by 20% and 15%, respectively, from the curve.

- Ensure linearity of the detector response using standards of motor oil and diesel and the single compound standards. Linearity must be within 15% for the motor oil and diesel standards and 10% for single compounds.
- The chemicals should be of reagent grade or better.
- Activated silica gel cleanup must be used on the samples.

In our case, the nC10, nC16, and nC34 response factors were checked on a per run basis as the GC/FID was not always used daily. Also, the silica gel cleanup was not employed. The silica gel cleanup is used to remove polar substances from the samples prior to analysis with the GC/FID; however, these are typically found in contaminated soil samples that have been subject to biodegradation [102, 103]. The synthetic hydrocarbon used in the drilling mud and present in the resulting waste is generated using a process specifically designed to minimize the concentration of polar molecules (refer to Section 3.1.1). Additionally, the waste was not subject to biodegradation; the sample was brought directly from an active drill site and placed in cold storage until it was used in the extractions.

The following list details the procedure used to calibrate the GC/FID used for this research. It should be noted that two calibrations were undertaken during this study; one at the start of the analysis in May 2006 and a second calibration in November 2006 after routine maintenance on the column. The procedures used for preparing and running standards on the GC/FID were the same in both cases.

1. A 500 mg·L^{-1} standard was prepared using approximately equal weights of nC10, nC16, and nC34 in toluene. Since nC34 is a crystalline solid, the solution was sonicated to ensure dissolution.
2. The 500 mg·L^{-1} standard was diluted using toluene to 250 mg·L^{-1}, 100 mg·L^{-1}, 25 mg·L^{-1}, 10 mg·L^{-1}, and 5 mg·L^{-1} standards (i.e. a 6-point calibration).
3. Each of the calibration standards was run through the GC/FID using the same conditions as used for the drilling waste samples (detailed in Table 3.2). Each was injected in triplicate.
4. The average response time was determined using the GC/FID software *Varian Star Chromatography Workstation (ver. 5.5)*. The area counts of the peaks were also determined using the same software.
5. Individual response factors were determined for each of the alkanes at each concentration for each of the triplicate injections. The response factor is calculated as [102]:

$$RF = \frac{A_{n-alk}}{C_{n-alk}}, \tag{8}$$

   where RF represents the response factor for the individual alkane; A_{n-alk} represents the area under the individual n-alkane peak; and C_{n-alk} represents the concentration of the individual n-alkane in the standard solution.
6. The average response factor as well as an overall average response factor for each alkane was determined. The linearity of the detector response of each of the

individual alkanes was also established by plotting the area count versus the known concentration and performing a linear regression. The results were compared to the CCME criteria [102].

7. An nC50 standard was prepared to a maximum concentration of 15 mg·L^{-1} in toluene. As with nC34, nC50 is a crystalline solid. Therefore, the standard was sonicated to ensure dissolution. The nC50 standard was injected in triplicate using the same GC/FID conditions as used for drilling waste samples (refer to step 3).
8. The retention time and response factor for nC50 was determined and compared to the CCME criteria, as per steps 4, 5 and 6.
9. Motor oil and diesel fuel standards were prepared by dissolving both in toluene at a 3:1 ratio. The standards prepared had an approximate total hydrocarbon concentration of 5,000 mg·L^{-1}, 10,000 mg·L^{-1}, and 50,000 mg·L^{-1}. A standard containing only diesel fuel was also prepared at a concentration of 10,000 mg·L^{-1}. Each of these standards was injected in triplicate using the same GC/FID program as used for drilling waste samples (refer to step 3).
10. The area count of the GC/FID output for each of the injections was determined and used to calculate the linearity of the response for the diesel fuel and motor oil standards. The linearity was compared to the CCME criteria.

3.2.2.2 Soxhlet Extraction and Quantitative Analysis using GC/FID

The CCME method recommends Soxhlet extraction to determine the total petroleum hydrocarbon content of a solid sample [102]. The following details the procedure used on the drilling waste samples before and after treatment with SFE and the subsequent quantitative analysis using GC/FID.

1. Approximately 5 g (dry weight) of drilling waste was weighed into a cellulose extraction thimble. The waste samples untreated with SFE were mixed with sodium sulphate until the sample was free-flowing. Each sample was extracted in triplicate.
2. The extraction used a 50:50 (by mass) n-hexane:acetone solvent mixture at a ratio of 20:1 with the dry soil. The extractions were performed for 16 to 24 hours with 4 to 6 solvent cycles per hour.
3. Once the extraction was complete, the solvent was recovered and passed through 9 g of 10-60 mesh sodium sulphate in a glass column to remove any water. The sodium sulphate was then rinsed with approximately 10 mL of n-hexane.
4. Using a rotary evaporator, the n-hexane:acetone solvent was evaporated from the sample. The sample was collected in a volumetric flask (typically 10 mL). The evaporation flask was rinsed with toluene; the rinsate was also added to the volumetric flask, which was then brought up to volume with toluene.
5. The sample from the volumetric flask was then filtered into a 2 mL GC/FID vial with crimp-top, Teflon® lined lid. The filter was a 0.45 μm, disposable Teflon® filter.
6. Two samples from each of the 2 mL samples was injected in the GC/FID. Using the average retention times and response factors determined through the calibration (refer to Section 3.2.2.1), the concentration of F2, F3, and F4 could be determined for the sample using Equations (9), (10), and (11):

$$C_{C10-C16} = \frac{\left(A_{C10-C16}\right)\left(V\right)\left(F\right)}{\left(RF_{avg}\right)\left(W_d\right)}, \tag{9}$$

$$C_{C16-C34} = \frac{(A_{C16-C34})(V)(F)}{(RF_{avg})(W_d)}, \tag{10}$$

$$C_{C34-C50} = \frac{(A_{C34-C50})(V)(F)}{(RF_{avg})(W_d)}, \tag{11}$$

where $C_{C10-C16}$, $C_{C16-C34}$, and $C_{C34-C50}$ represent the concentration of hydrocarbon in the sample for the indicated range (mg hydrocarbon/kg sample); $A_{C10-C16}$, $A_{C16-C34}$, and $A_{C34-C50}$ represent the integration of all area counts from the retention time of the first carbon number to the retention time of the second carbon number; V represents the final volume of the sample extract (mL), typically 10 mL in this case; F represents the dilution factor used to bring the samples within the peak height range of the calibration standards; RF_{avg} represents the total average response factor; and W_d represents the dry weight of the sample (g). The dry weight of the sample was determined using the following equation:

$$W_d = W(1-f), \tag{12}$$

where W_d represents the dry weight of the sample (g); W represents the weight of the sample (g); and f represents the fraction of water in the sample (g water/g of sample). For the untreated waste samples, the fraction of water in the sample was determined through a Dean and Stark analysis, conducted at a commercial laboratory (discussed in detail Section 4.2.2). For the treated samples, the water content was assumed to be negligible.

7. The extraction efficiency of the SFE run was determined using two methods. First, the extraction efficiency was calculated using the mass of hydrocarbons collected in the separator vials, according to Equation (13):

$$E_{mass} = \frac{f\left(m_{sample}\right) - m_{collected}}{f\left(m_{sample}\right)} \times 100, \tag{13}$$

where E_{mass} represents the extraction efficiency based on the mass of hydrocarbons collected, in percent; f represents the fraction of hydrocarbons in the initial sample of untreated waste, as determined by Soxhlet extraction; m_{sample} represents the mass of the drilling waste sample treated in the extraction, in grams; and $m_{collected}$ represents the mass of hydrocarbons collected in the separator vials. Second, the extraction efficiency is calculated according to the results of the CCME analysis, using Equation (14):

$$E_{CCME} = \frac{PHC_{untreated} - PHC_{treated}}{PHC_{treated}} \times 100, \tag{14}$$

where E_{CCME} represents the extraction efficiency according to the CCME analysis, in percent; $PHC_{untreated}$ is the petroleum hydrocarbon content of the untreated sample determined by CCME analysis, in $\mathrm{mg{\cdot}kg^{-1}}$; and $PHC_{treated}$ is the petroleum hydrocarbon content of the treated sample determined by CCME analysis, in $\mathrm{mg{\cdot}kg^{-1}}$.

CHAPTER 4 - RESULTS AND DISCUSSION

4.1 Data Collection from SFE System

Every ten seconds during an extraction, data is recorded for the pump pressure, the vessel pressure, the CO_2 flow rate from the pumps, and the vessel temperature. The collected data is discussed in the following sections. A sample of the output from the data acquisition software is provided in Appendix A.

4.1.1 Pressure Data

Figure 4.1 highlights the pressure data collected from the pumps and the pressure transducer at the vessel for a typical extraction.

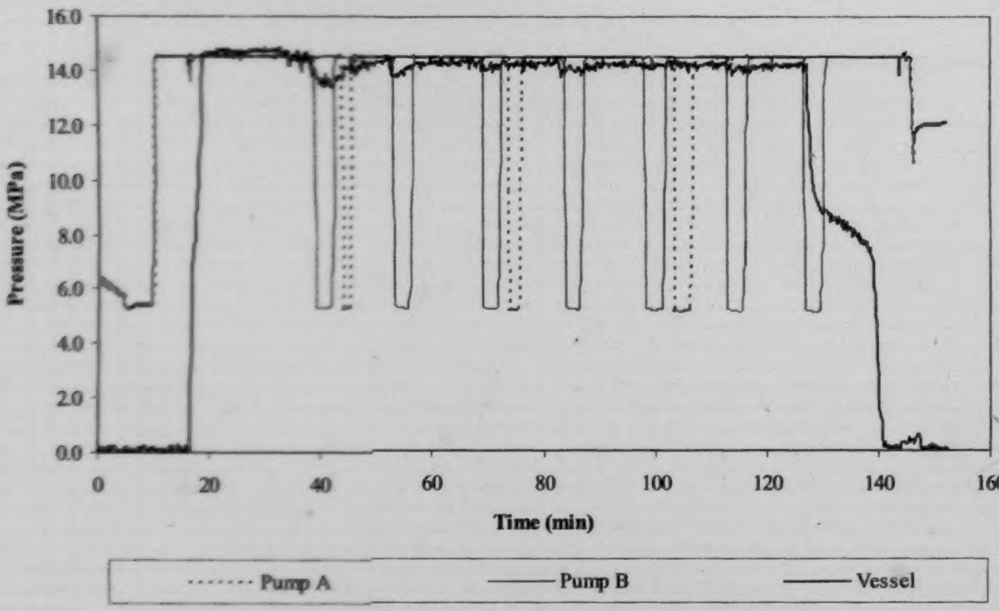


Figure 4.1 **Typical pressure data collected for pumps and vessel**

In the initial part of Figure 4.1 (from 0 to 9.5 minutes) the vessel registers ambient pressure and the pumps register the pressure in the cylinders remaining from a previous run. At 9.5 minutes, the pumps are refilled and pressurized to the desired extraction pressure of 14.5 MPa. Around 16.5 minutes, the valve allowing pressurized CO_2 to flow to the vessel is opened and the vessel is pressurized to 14.5 MPa. The next 15 minutes represents the static period where no CO_2 flows in or out of the vessel. At approximately 31 minutes, the dynamic phase begins and the vessel outlet valve is opened (represented by a slight drop in vessel pressure). Through the dynamic phase, the pumps are set to supply CO_2 continuously at a pressure of 14.5 MPa to the vessel. As the pumps are emptied throughout the extraction, they are stopped and refilled as shown in the figure as drops in pressure to the cylinder pressure. However, the pumps are arranged in a parallel fashion, allowing one pump to provide CO_2 at 14.5 MPa while the other is refilled and repressurized.

The variation in pressure at the vessel is a result of fine tuning of the CO_2 flow rate at the metering valve; all attempts are made to maintain a constant flow rate through the system while the pumps are providing SC CO_2 at 14.5 MPa. The pumps are effectively 'pushing' against the metering valve and small adjustments to control flow rate cause a delayed reaction at the pumps and, therefore, a pressure change in the vessel.

4.1.2 Temperature Data

Figure 4.2 shows the temperature data collected from the thermistor in the extraction vessel during a typical extraction run. The set point of 40°C is shown as a dashed line in the figure.

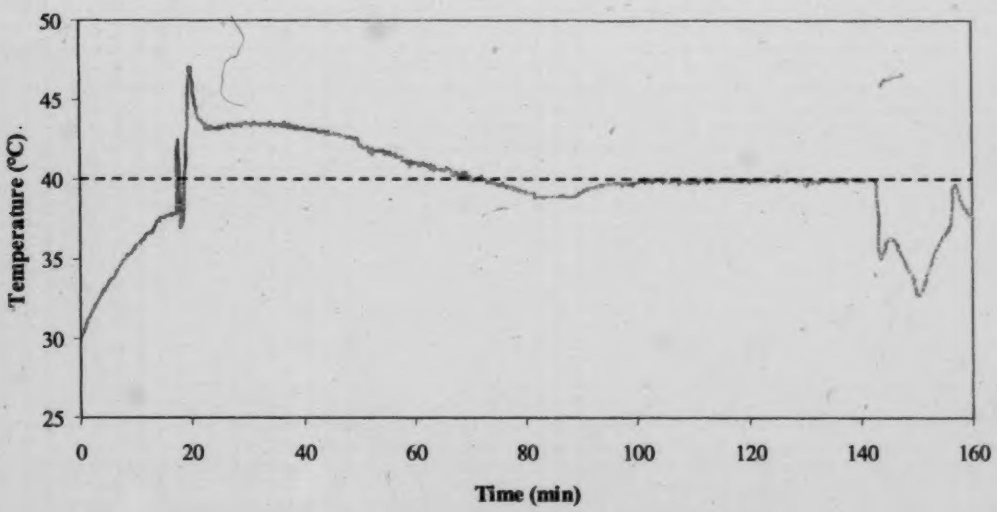


Figure 4.2 **Typical temperature data collected from the vessel thermistor**

For approximately the first 20 minutes of the run, the vessel was heated to approximately 40°C using water from the hot water bath circulated to the jacket surrounding the vessel. Once the static period begins at about 20 minutes, the temperature measured in the vessel jumps to approximately 47°C. The jump in temperature is due to the influx of warmed CO_2 from the coiled inlet line that is also situated in the hot water bath. The temperature of the vessel slowly decreases throughout the static period (from approximately 20 to 35 minutes) and the early part of the dynamic period. The flow of CO_2 from the pumps (the pumps are cooled to 7.5°C) causes a decrease in both the vessel temperature and the hot water bath temperature. Once the temperature of the hot water bath drops below the set point, observed as a brief dip the vessel thermistor reading, the circulator heating element turns on and begins heating the water to the set point of 40°C. The vessel thermistor reading remains at approximately 40°C until the end of the run when the circulator is turned off. For the run shown in Figure 4.2, the average vessel temperature was 40.8 ± 1.7°C. The temperature profile shown is typical of all the extraction runs performed.

4.1.3 Carbon Dioxide Flow Rate Data

Figure 4.3 shows the typical flow rate data collected from each pump during a typical extraction. It should be noted that these flow rates are as measured at the pumps (7.5°C and 14.5 MPa).

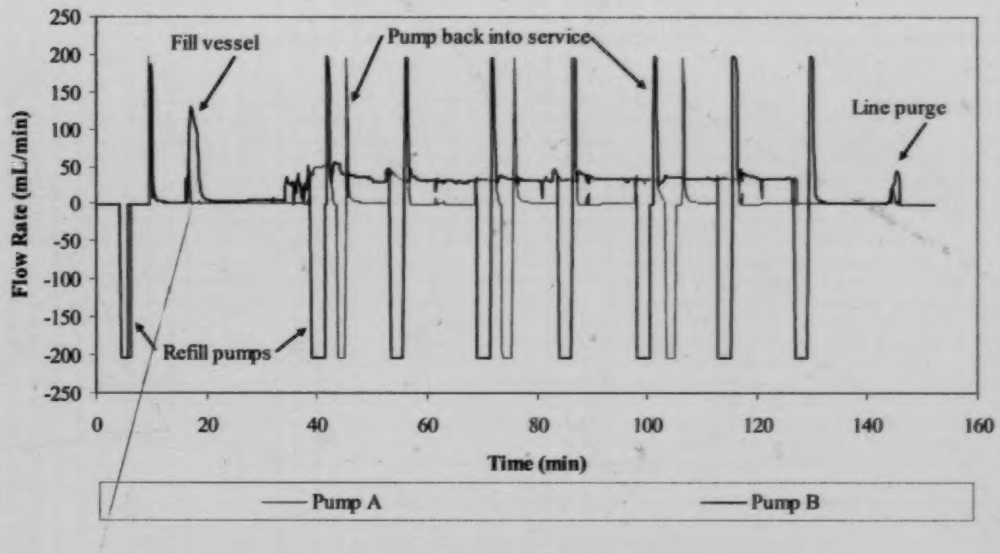


Figure 4.3 Typical flow rate data collected for pumps

As can be seen in the Figure 4.3, the CO_2 flow rate begins at zero. Before the extraction can begin, the pumps must be refilled with CO_2. Refilling is recorded as a negative flow rate (approximately -215 $mL \cdot min^{-1}$). As the pumps are pressurized, a spike to around 200 $mL \cdot min^{-1}$ is observed; this is a small flow representing the pressurization of the short length of tubing from the pumps to the first control valve.

Once the pumps are pressurized, the extraction can begin and the valves are opened to allow the pressurized CO_2 to flow into the vessel (valves 4 and 6 in Figure 3.6). This flow is shown as approximately 125 $mL \cdot min^{-1}$ in Figure 4.3. There is no flow from the pumps during the static period (from 22 to 37 minutes).

Then the outlet valves are opened (valves 13 and 14 in Figure 3.6) and the dynamic phase begins. During the dynamic phase, pump B runs as the main pump and pump A runs as a backup. Pump B begins flowing CO_2 at about 30 $mL \cdot min^{-1}$. Once pump B is empty, it is refilled, as indicated by the negative flow. When pump B is refilled, pump A automatically takes over at the same flow rate. As pump B is put back into service, there is a spike in flow rate as it 'pushes' against the metering valve to achieve the set pressure (14.5 MPa). At the same time, the flow from pump A slowly drops off. Pump A is then also refilled so that it may sit as back up for when pump B is empty and refilled again.

At the end of the extraction, flow is allowed to proceed directly from the pumps through the bypass lines (3-way valve 6 in Figure 3.6 is closed to the vessel and opened directly to valves 13 and 14). The purpose of bypass flow is to purge any hydrocarbons that may have been deposited in the lines during depressurization. The bypass flow is indicated in Figure 4.3 as the line purge.

The flow rate through the system can be difficult to control. On the figure, this difficulty manifests as small variations in flow rate during the times in between refilling and repressurizing the pumps; the time when the pump is flowing CO_2 through the system. These variations arise due to the movement of hydrocarbon and/or potentially entrained solids through the system. It can be particularly difficult in the early part of the dynamic phase as more hydrocarbons are extracted. All attempts are made to maintain a constant flow rate through the system by slight adjustments of the metering valve.

4.2 Petroleum Hydrocarbon Analysis

As discussed in Section 3.2.2, the hydrocarbon content of the centrifuge underflow drilling waste was determined before and after extraction with SC CO_2 using the CCME method [102]. While the CCME method document details procedures for the full range of hydrocarbons from F1 to F4, the range of carbon numbers of the drilling waste hydrocarbons only requires a determination of total petroleum hydrocarbons in the F2 to F4 range (carbon numbers C10 to C50). For C10 to C50, CCME requires the use of Soxhlet extraction followed by quantitative analysis using GC/FID.

The following sections detail the GC/FID calibration results and the extraction efficiency of the SFE runs as determined through Soxhlet and GC/FID. The results include the hydrocarbon content of the waste prior to the extraction, a summary and description of the SFE runs performed, and the hydrocarbon content of the treated waste.

4.2.1 Gas Chromatography Calibration

Two calibrations were performed using the procedure highlighted in Section 3.2.2.1. The first calibration was completed in May 2006 and is valid for GC/FID runs up until the second calibration completed in November 2006. The second calibration became necessary after performing routine maintenance of the GC/FID column in order to maintain the quality control and quality assurance guidelines indicated in the CCME method.

4.2.1.1 Individual Alkane Standards

Standard solution mixtures containing C10, C16, and C34 each at 5 mg·L^{-1}, 10 mg·L^{-1}, 25 mg·L^{-1}, 100 mg·L^{-1}, 250 mg·L^{-1}, and 500 mg·L^{-1} in toluene were prepared. Figure 4.4 shows the typical FID response and the retention time for one of these solutions. Figure 4.5 shows the typical detector response and retention time for a standard solution of C50. Because C50 has a limited solubility in toluene, it was not included in the C10, C16, and C34 mixture and was only prepared at 10 mg·L^{-1}. In both figures, the large peak present in the early part of the detector response (from 0.5 to 3 minutes) is the solvent (toluene) peak.

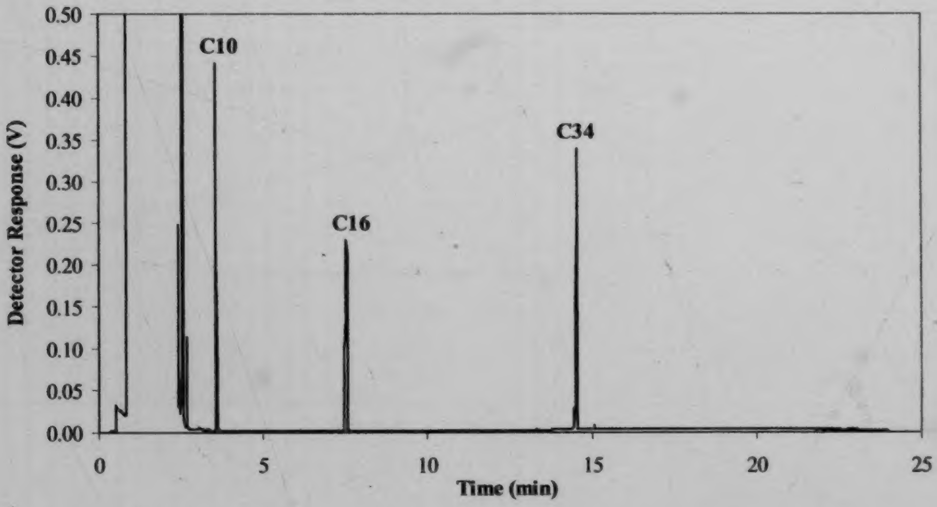


Figure 4.4 Typical GC/FID output showing C10, C16, and C34 peaks

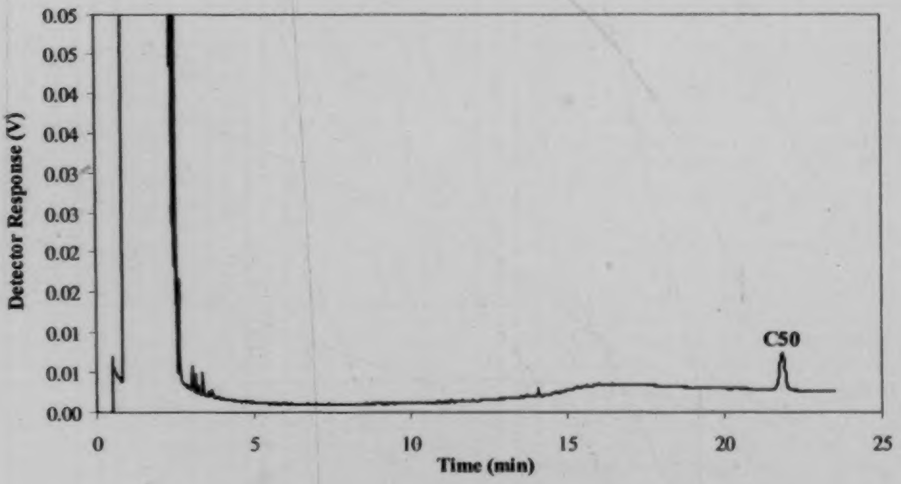


Figure 4.5 **Typical GC/FID out put showing C50 peak**

Each sample of standard solution was injected in triplicate. The GC/FID software package, *Varian Star Chromatography Workstation (ver. 5.5)*, was used to determine the area counts under the individual alkane peaks. The results of these runs are shown in Figure 4.6 and Figure 4.7. CCME quality criterion requires linearity of the detector response within 90% for the individual alkanes. Linearity was established using the linear regression feature in MS Excel. The linear correlation factor for the individual compounds (R^2) is shown on the figures. If the R^2 values are greater than 0.90, the CCME criterion is deemed to be met.

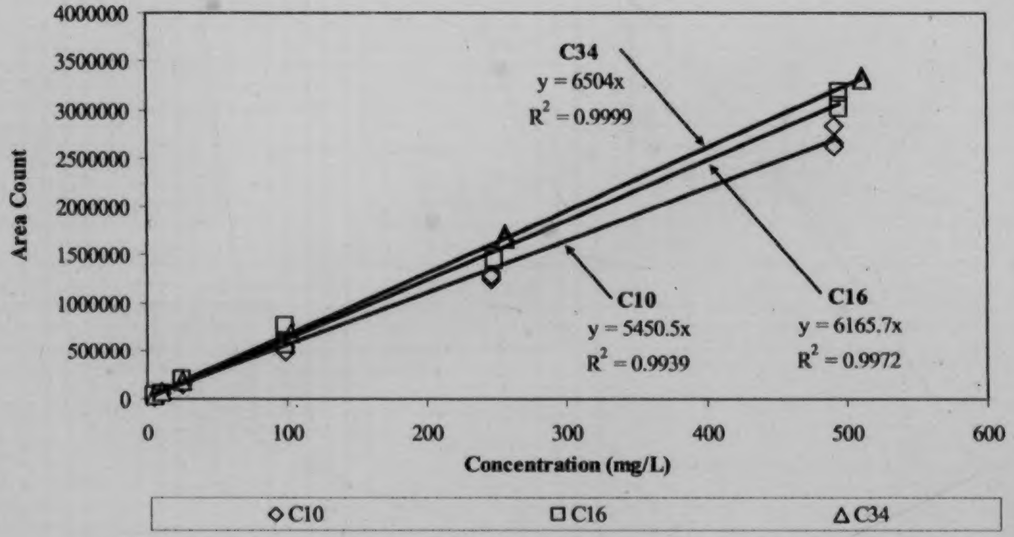


Figure 4.6 May 2006 GC/FID calibration curve, individual alkanes

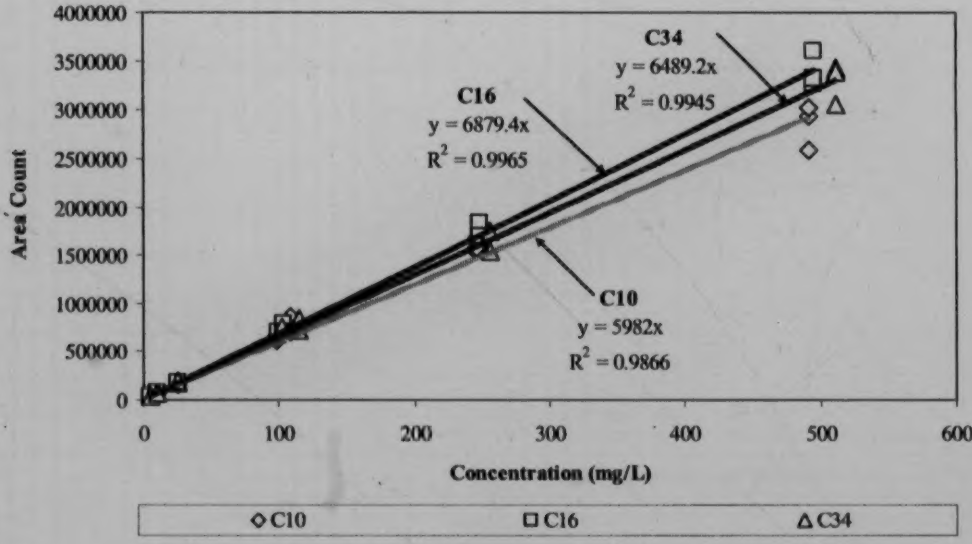


Figure 4.7 November 2006 GC/FID calibration curve, individual alkanes

Response factors for each alkane were calculated according to the CCME method described in Section 3.2.2. The results are shown and compared to the CCME quality criteria in Table 4.1. For the calibration to meet CCME quality criteria, the response factors for C10, C16, and C34 must be within 10% of each other as determined by a percent error in comparison with the average response factor. Also included in Table 4.1 is the response factor for C50 which must be within 30% of the average response factor. The average response factor from each calibration was later used to determine the total hydrocarbon content of the drilling waste samples.

Table 4.1 Calibration response factors and comparison to CCME quality criteria

Alkane	Response Factor May 2006	Response Factor November 2006	Error (%) May 2006	Error (%) November 2006	CCME Criteria[102]
C10	5716.6	6401.6	6.4	4.2	<10
C16	6125.4	6754.6	0.2	1.1	<10
C34	6490.1	6883.3	6.2	3.2	<10
C50	5878.9	5948.7	3.8	10.9	<30
Average	6110.7	6679.8	-	-	-

The average retention times for each of the alkanes was also determined and the results are given in Table 4.2. These retention times were later used to delineate the F2 (C10 - C16), F3 (C16 - C34), and F4 (C34 - C50) fractions to determine area counts for the diesel and motor oil standards as well as the drilling waste samples.

Table 4.2 Average retention times for C10, C16, C34, and C50

Alkane	Retention Time (minutes) May 2006	Retention Time (minutes) November 2006
C10	3.60	3.55
C16	7.60	7.54
C34	14.62	14.55
C50	22.58	22.29

4.2.1.2 Diesel and Motor Oil Standards

The CCME method also requires that the GC/FID be calibrated using solutions of known concentrations of petroleum products. For the May and November calibrations, solutions of diesel and motor oil containing a total hydrocarbon content of 1,000 mg·L^{-1}, 5,000 mg·L^{-1}, 10,000 mg·L^{-1}, and 50,000 mg·L^{-1} were prepared. Additionally, a single solution consisting of only diesel was prepared at a concentration of 10,000 mg·L^{-1}. Typical GC/FID chromatographs of these solutions are shown in Figure 4.8.

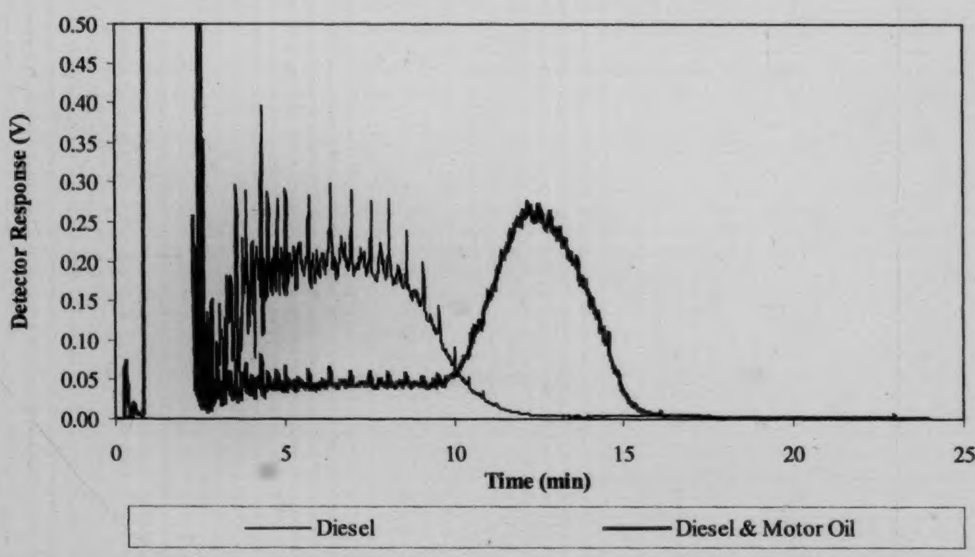


Figure 4.8 Typical GC/FID output showing diesel and diesel/motor oil standards

In order to meet CCME quality specifications for GC/FID, the diesel and diesel/motor oil standards must have a linear relationship between area count and known concentration, as shown in Figure 4.9. To prepare Figure 4.9, the average retention times (from Table 4.2) were used to delineate the F2 (C10 – C16), F3 (C16 – C34), and F4 (C34 – C50) hydrocarbon ranges. Using the group peak function in the *Varian Star*

Chromatography Workstation (ver 5.5) software, the area count for each of these ranges was determined (refer to Appendix B for a software sample report). The plots in Figure 4.9 represent the area count versus the known total petroleum hydrocarbon content of the diesel and diesel/motor oil (sum of the F2, F3, and F4 area counts). The CCME quality criterion requires that the linearity to be 0.85 or larger. The linear correlation factor, R^2, from the MS Excel linear regression function was used to determine linearity. As can be seen from the calibration plots, both the May and November R^2 values exceed the 0.85 requirement.

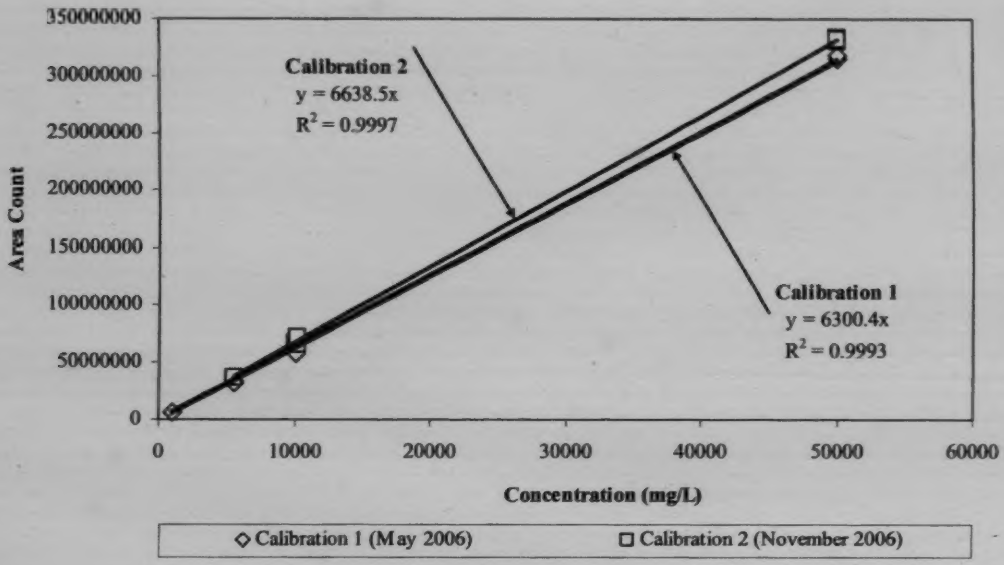


Figure 4.9 Linearity check for diesel and diesel/motor oil standards

4.2.2 Untreated Waste Hydrocarbon Content

In order to determine the efficiency of the supercritical fluid extractions in this research, first the initial hydrocarbon content of the centrifuge underflow drilling waste, described in Section 3.1.1, had to be determined.

Using the CCME analysis as described in Section 3.2.2, the average hydrocarbon content of the synthetic-based, centrifuge underflow drilling waste was determined to be 12.7% ± 1.4% (dry weight). This result is the average of eighteen Soxhlet extractions injected in duplicate in the GC/FID.

In addition to the analysis performed in-house, a sample of the untreated drilling waste was also sent to Norwest Labs of Edmonton, Alberta, Canada where the oil content was determined to be 15.3% ± 1.0% (dry weight). As the "SFE treated" samples are also analysed using the CCME method, only the CCME result of 12.7% was used to calculate and compare SFE efficiencies. The result from Norwest Labs was only used to confirm the untreated waste hydrocarbon content from the CCME method. The variance in the two is likely a result of the analysis methods used; the CCME method employs a Soxhlet extraction while Norwest Labs employs the Dean and Stark method to determine oil, water, and solids content. The Soxhlet extraction is not able to directly determine the water content of the sample.

These results are also similar to those reported in other SFE studies on various types of hydrocarbon contaminated drilling wastes including Lopez Gomez [21] (19.4% and 14.8%), Odusanya [22] (17.2%), Saintpere and Morillon-Jeanmaire [104] (6% to 13%) and Seaton and Hall [25] (4.5% to 13.5%).

The Dean and Stark analysis completed at Norwest Labs also determines the water content of the sample. The water content is used in determining the efficiency of the extractions using the CCME analysis. The water content of the untreated waste sample was determined to be 3.1% ± 0.7%.

4.2.3 Treated Waste Hydrocarbon Content and Extraction Efficiency

As described in the research objectives, the purpose of this SFE study was to continue the research previously undertaken at the University of Alberta using SC CO_2 to extract hydrocarbons from drilling waste. In this study, the determined optimum conditions from the previous research by Lopez Gomez [21] were used as a starting point to be applied to a different drilling waste samples. Rather than adjusting the pressure and temperature of the extraction, adjustments were made to fine-tune the process by solving some of the problems encountered in previous studies, such as solids carryover and the limited amount of waste that could be treated. The following sections summarize the SFE runs completed and the pertinent results obtained. Table 4.3 lists the research results.

The additives used in some runs listed in Table 4.3, indicated by A1 and A2, are solid substances. The specific chemical constituents of each of the additives are not given in this thesis due to their commercialization potential. However, inquiries regarding their nature and composition can be made to the thesis author.

Each experimental run, numbered in Table 4.3 from 1 to 18, resulted in treated waste which was analysed for total petroleum hydrocarbon content using the CCME method. Three sub-samples were taken from each treated waste sample for Soxhlet extraction. The resulting solvent from the Soxhlet extraction was injected into the GC/FID for analysis in duplicate. Therefore, for each run indicated in the Table 4.3, the results are the average of six GC/FID injections. A standard deviation was also calculated for the results of the CCME analysis on the treated waste samples, as shown in Table 4.3. Variability in the results, as shown by high standard deviations on some runs, is thought to be caused by uneven distribution of hydrocarbon concentrated solids in the samples used for the Soxhlet extraction. In some of the runs, particularly those involving higher masses of waste or without the use of an additive, the resulting treated waste contained ‘chunks’ of solids with a higher concentration of hydrocarbon in their interior. While all attempts were made to break up and evenly distribute these chunks, on occasion some of these chunks may have been present in some samples and not in others.

The efficiency results from the CCME results were also verified using the mass of hydrocarbon collected during the extraction. As can be seen Table 4.3, the extraction efficiency results based on the mass of hydrocarbons collected, in some instances, show a large variability between identical runs and are also quite different than those using the CCME method. The variability is due to how the hydrocarbons are collected for mass analysis. The flow of CO_2 often pushes hydrocarbon from the sample vials and in some runs the glass beads and/or glass wool have also been lost from the vials. In some of the runs, a large amount of solids are carried into the sample vials from the vessel. Also, on occasion, some of the water from the ice water bath also entered the sample vials. Again, the mass results are used strictly for verification purposes and may be higher or lower than the extraction efficiencies calculated by the CCME analysis due to the aforementioned factors.

Table 4.3 Summary of total petroleum hydrocarbon content and extraction efficiencies from SFE with SC CO_2 at 14.5 MPa and 40°C

No.	Mass (g)	Flow ($g \cdot min^{-1}$)[1]	Outlet Modification (Yes/No)	Mixer Speed (rpm)	Additive		Hydrocarbon Content (%)		Extraction Efficiency (%)	
					Type	Mass (g)	CCME Method	SD	Mass HC Collected	CCME Method
1	75.12	18.5	N	50	-	-	3.49	0.45	74.6	72.6
2	72.84	17.2	N	50	-	-	2.68	0.30	79.5	79.0
3	48.74	14.9	N	50	A1	3.23	0.32	0.03	98.3	97.5
4	62.30	19.0	N	50	A1	5.09	0.18	0.01	97.3	98.6
5	53.45	19.6	Y	50	-	-	2.19	0.09	92.6	82.8
6	49.77	19.1	Y	50	-	-	2.54	0.28	85.6	80.1
7	49.83	32.3	Y	50	-	-	2.07	0.13	79.3	83.8
8	50.40	30.7	Y	50	-	-	1.72	0.08	70.1	86.5
9	50.62	36.3	Y	50	-	-	2.06	0.36	96.5	83.8
10	49.97	27.2	Y	50	A2	14.14	0.80	0.47	102.8	93.7
11	51.43	33.9	Y	50	A2	14.47	0.29	0.12	72.4	97.7
12	50.58	34.4	Y	50	A2	14.30	0.12	0.01	106.9	99.1
13	102.60	40.3	Y	50	A2	28.87	2.41	0.25	92.3	81.1
14	99.66	37.9	Y	50	A2	28.24	0.41	0.04	70.4	96.8
15	99.58	35.3	Y	50	A2	28.19	0.18	0.02	104.4	98.6
16	149.14	39.8	Y	50	A2	42.50	3.32	0.18	35.7	73.9
17	151.52	35.3	Y	100	A2	42.89	4.78	0.26	68.8	62.5
18	150.34	38.1	Y	100	A2	42.69	6.10	0.16	61.2	52.1

[1] *Flow* – average over dynamic phase, converted from $mL \cdot min^{-1}$ to $g \cdot min^{-1}$ using a CO_2 density of 0.96316 $g \cdot mL^{-1}$ from *Thermophysical Properties of Fluid Systems* database provided by NIST [105]

4.2.3.1 Initial Extractions

Experimental runs 1 and 2 in Table 4.3 show the results of the first successful extractions completed using the previously described optimum conditions from Lopez Gomez [21]. However, nearly seven SFE runs were attempted before these first results could be obtained. In the earlier research, Lopez Gomez extracted 100 g of diesel oil-based centrifuge underflow cuttings at 14.5 MPa and 40°C using a mixing speed of 800 rpm and a CO_2 flow rate at the pumps of 9.6 to 11.6 g·min^{-1} [21]. Under these conditions, the clay-like solids in the synthetic-based centrifuge underflow waste severely clogged the downstream lines and valves.

Strictly through trial-and-error, the mass of waste treated and the mixing speed were adjusted to limit (though did not completely eliminate) the movement of solids from the vessel into the downstream lines. The first successful runs were completed at the same SC CO_2 density but with only 75 g of waste and a mixing speed of 50 rpm. The resulting treated sample was dry, light in colour, and had slightly flaky chunks present. These initial successful extractions resulted in a reduction in total hydrocarbon content from 12.7% to an average of 3.1%. The average extraction efficiency was 75.8% for the two runs.

As shown previously in Section 3.1.3, the ribbon blender used in the process moves the solids in an upward motion in the vessel. Mixing provides excellent contact between the solids and the SC CO_2, but causes issues at the outlet that is located at the top of the vessel, becomes prone to clogging (see to Figure 4.10). At 800 rpm, the solids are effectively forced against the lid of the vessel and into the outlet port. The outlet clogging problem seems to be more pronounced with the synthetic-based underflow waste in comparison with the diesel-based underflow waste used by Lopez Gomez [21]. Decreasing the total mass of solids in the vessel and decreasing the mixing speed allowed for a successful extraction without clogging. Another advantage to reducing the mixing speed is a reduction in the power requirements of the system. While not a major issue considering this is a lab scale system, it would affect the economics of the process for a larger scale system.

Figure 4.10 **Photo showing the extraction vessel outlet port clogged with fine solids from the waste, approximate scale 1:1**

While the results were encouraging, previous studies were able to achieve much higher extraction efficiencies (98%) [21]. Because of the necessary reduction in mixing speed in the vessel, there was a reduction in contact between the SC CO_2 and the waste. The reduction in contact corresponded to a reduction in extraction efficiency, which is similar to the channeling problems described by Seaton and Hall [25]. The mixing speed could not be increased, so alternative methods of increasing contact between the SC CO_2

and the waste were tested. A waste additive was used in the subsequent set of experiments, and the results are described in the following section.

4.2.3.2 Effect of Additive A1

Extraction runs 3 and 4 on Table 4.3 show the results from the runs completed using additive A1, which was mixed with the waste prior to introducing it to the extraction vessel. The mass of waste treated was reduced to approximately 50 g because it was unknown how much A1 would be required and also, as determined in runs 1 and 2, the maximum amount of solids in the vessel (waste plus additive) should be 75 g or less. The amount of A1 required was determined first in run 3 strictly by visual observation. The ratio of additive to waste was determined and then used to determine the amount of additive to use in run 4, for consistency. The additive to waste ratio for these runs was 0.07 on average on a mass basis.

The extraction efficiencies of the runs with A1 were much better than the extraction efficiencies of the previous runs. Visually, the treated waste was dry, light in colour, and free flowing with no chunks present. The average hydrocarbon content of the treated waste was 0.25% and the average extraction efficiency was 98.1%. It should be noted that 0.25% is well below the hydrocarbon limit for release of synthetic-based drilling waste solids to sea (6.9 g per 100 g of waste solids, refer to Section 2.2.1) and also half the required hydrocarbon content for site closure in an onshore, Alberta land treatment operation (0.5% in the topsoil layer, refer to Section 2.2.3.1).

Although A1 clearly improved the process by increasing the contact between the waste and the SC CO_2 during extraction, there is a concern that the presence of A1 in the treated waste would prevent regulators from allowing it to be released directly to the environment, which is the ultimate goal of SFE treatment of hydrocarbon contaminated drilling wastes. Additionally, A1 provided no improvement over runs 1 and 2 in terms of the amount of solids being carried into the downstream lines and sample vials. As such, further investigations were undertaken to test other process modifications and additives.

4.2.3.3 Effect of Outlet Modification

Even with a reduced waste mass and mixing speed, the system was still prone to solids carryover from the vessel. In order to prevent solids carryover, a Teflon® barrier, approximately 1 mm in thickness, was constructed to act as a physical separation between the bulk waste and the outlet. Teflon® was used because it is a non-reactive material, and because it easily allows the SC CO_2 to pass into and out of the vessel. The outlet modification design is shown below in Figure 4.11.

Figure 4.11 Teflon® outlet modification design, approximate scale 2:1

In order to test the effect of the vessel outlet modification only, no additives were used. The results of the first runs completed with the modification are shown as runs 5 and 6 in Table 4.3. Not unexpectedly, the results for these two runs are similar to runs 1 and 2 in which no additive was employed. The average hydrocarbon content for runs 5 and 6 was 2.72% resulting in an average extraction efficiency of 81.5%. Visually there were less solids carried over into the sample vials. With a reduction in solids entrainment, the flow control of the system using the metering valve (valve 14 in Figure 3.6) was much less variable.

In order to fully test the effectiveness of the barrier, a second set of runs (7 to 9 in the table) were completed at a higher SC CO_2 flow rate. Increasing the flow of SC CO_2 through the vessel (28.9 to 38.5 $g{\cdot}min^{-1}$ versus the low flow of 9.6 to 19.3 $g{\cdot}min^{-1}$) increases the likelihood of solids carryover. Again, the extraction efficiency and hydrocarbon content results are similar to those from runs 1, 2, 5, and 6. However, the effectiveness of the barrier can be qualitatively observed in Figure 4.12. The sample vial on the left was the first sample vial from run 2, completed without the outlet modification and at a low flow rate. Clearly, the collected hydrocarbon is contaminated with fine solids. In comparison with the vial on the right of Figure 4.12, the first vial from run 7 completed with the outlet modification in place and at a higher flow rate, the collected hydrocarbon showed no solids and is visibly cleaner.

Figure 4.12 Photo showing first sample vial from runs without (left) and with (right) the outlet modification in place, approximate scale 2:1

There is an added benefit, also, of completing runs at a higher flow rate. As SFE is a batch process, it is advantageous to reduce the time required to complete a run to the desired efficiency. This result is shown graphically in Figure 4.13.

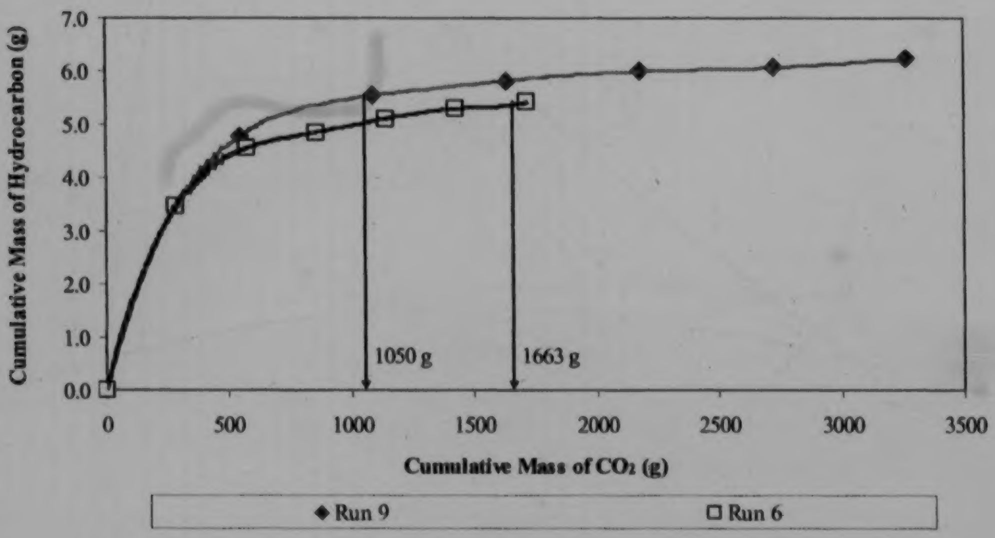


Figure 4.13 **Cumulative mass of hydrocarbon collected versus the cumulative mass of CO_2 used in the extraction**

Figure 4.13 shows the cumulative mass of hydrocarbons collected in the sample vials over the dynamic phase of the extraction run, indicated by the cumulative mass of CO_2 used, as measured at the pumps (7.5°C, 14.5 MPa). Runs 6 and 9, from Table 4.3, were chosen in generating Figure 4.13 because they were similar in extraction conditions except for their flow rates. Run 6 had an average flow rate of 19.1 $g{\cdot}min^{-1}$ and Run 9 had an average flow rate of 36.3 $g{\cdot}min^{-1}$. The vertical arrows on Figure 4.13 indicate the location of an arbitrary extraction efficiency for comparison of each of the runs (85% in this case). From Figure 4.13 it can be determined that Run 9, with a higher CO_2 flow rate, achieved 85% extraction efficiency using 1050 g of CO_2 in comparison with Run 6 which used 1663 g of CO_2. Therefore, the higher flow rate resulted in a faster and more efficient run in terms of mass of CO_2 used.

Because the outlet modification was able to eliminate the solids carryover at the high flow rate, both the modification and high flow rate were used in the remaining runs shown in Table 4.3. However, the outlet modification and the increase in flow rate did not increase the final extraction efficiencies because neither affected the contact between the SC CO_2 and the waste. Visually the drilling waste treated at a high flow rate and with the outlet modification in place was chunky; visibly clean and dry on the exterior of the chunk but clearly darker on the interior, indicating the presence of hydrocarbon.

4.2.3.4 Effect of Additive A2

Based on the results from the additive A1 runs, it became obvious that an additive would increase the contact between the SC CO_2 and the hydrocarbon in the waste thereby increasing the extraction efficiency. However, there are potential environmental concerns with the use of A1. Therefore, investigations were carried out to develop a second, more "natural" additive to address these concerns.

As with the runs completed with A1, only 50 g of drilling waste was used to avoid exceeding the currently determined 75 g limit. The additive to waste ratio was calculated and applied to runs 11 to 18. The average additive to waste ratio was 0.29 by mass for the runs using A2.

For runs 10 to 12, completed with 50 g of waste, the average total hydrocarbon content for the treated solids was 0.40% and the average extraction efficiency was 96.8%. Visually, the solids were dry, light in colour, with no chunks of concentrated hydrocarbon. With the outlet modification in place, no solids carried over into the sample vials.

As with the A1 results, the hydrocarbon content is well below the limit for offshore discharge or closure of a land treatment site. However, the use of A2 does not present issues with releasing the solids to the environment as A1 would. The only drawback to A2 is that a larger mass is needed in comparison with A1. Recall that the waste to additive ratio for A2 and A1 are 0.29 and 0.07 by mass, respectively.

The second set of runs completed using A2 are runs 13 to 15 in Table 4.3. Because the system performed well in runs 10 to 12, an attempt was made to determine the maximum mass that the system could handle without clogging now that the outlet modification's effectiveness was proven and an additive had been used that could produce favourable results. For runs 13 to 15 about 100 g of waste plus A2 was placed in the vessel, for a total mass of around 130 g. The average total hydrocarbon content for these runs was 1.0% and the average extraction efficiency was 92.2%. These results are still below the allowable 6.9 g per 100 g for offshore environmental release but are above the 0.5% required for site closure of a land treatment operation in Alberta. The benefit of treating more waste per run is obvious when one considers the batch nature of SFE.

While the extraction efficiences were slightly lower than for the 50 g experiments, the 100 g experiments produced treated waste with a low final hydrocarbon content. Also, there were no process problems encountered during the 100 g runs; the outlet modification prevented any solids carryover and clogging in the downstream lines. Therefore, in order to determine the limit of mass that could be accommodated by the extraction vessel, a third set of experiments was completed using about 150 g of waste (about 200 g total including additive), indicated as runs 16 to 18 in Table 4.3.

The first of these runs, run 16, was completed with the mixer at 50 rpm. No solids carryover or clogging was observed. The total hydrocarbon content of the treated waste was 3.32% but, interestingly, the colour of the treated waste solids was stratified within the vessel (see Figure 4.14). That is, the solids at the top of the vessel nearest to the inlet and outlet ports were dry and light in colour while the solids at the bottom of the vessel were still dark in colour. The solids at the bottom of the vessel clearly had not had sufficient contact with the SC CO_2. In Figure 4.14, the solids were inverted from the vessel to the sample jar so the darker, less treated solids that were at the bottom of the vessel are at the top of the jar.

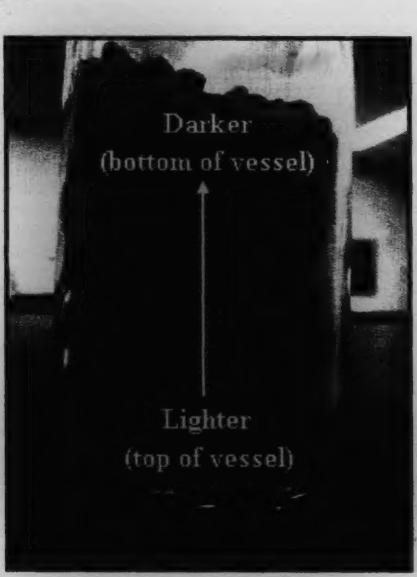


Figure 4.14 **Photo showing stratification of solids from the vessel, approximate scale 1:1**

As no solids carryover or clogging had been observed, runs 17 and 18 were completed with the mixer at 100 rpm to increase the movement of the waste in the vessel. However, these runs were subject to significant solids carryover and clogging; so much so that only two runs could be fully completed. The average total hydrocarbon content of the runs was 5.44% with an average extraction efficiency of 57.3%. Visual observation revealed that even at 100 rpm the colour of the treated solids was still stratified as Figure

4.14. Based upon these results, the total maximum capacity of the lab scale vessel is approximately 150 g.

4.2.4 Gas Chromatography Comparison

One of the main conclusions of most SFE studies involving the extraction of hydrocarbons from drilling waste is that the hydrocarbon is unchanged by the extraction process [21, 22, 25]. Figure 4.15 shows the detector response for the GC/FID analysis of the hydrocarbon in the synthetic-based centrifuge underflow waste used in this study before and after extraction with SC CO_2. The important result to note from the figure is not the magnitude of the detector response; instead, compare the location and relative magnitude of the peaks within the total hydrocarbon response. Based solely upon visual observation, the location and size of these peaks indicates that the hydrocarbon profile is not altered by the interaction with the SC CO_2.

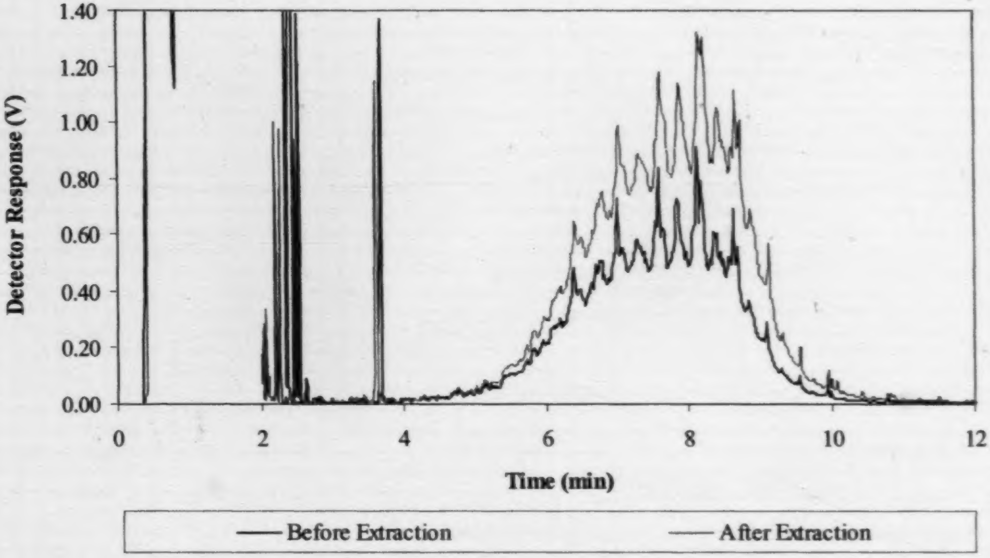


Figure 4.15 GC/FID output showing detector response from drilling waste hydrocarbon before and after extraction with SC CO_2

This result confirms the conclusions of previous studies and is an important conclusion because one of the main advantages of treating hydrocarbon based drilling waste using SFE is that the hydrocarbon is recovered from the process, unlike, for example, biological treatment methods where the hydrocarbon is consumed in the process. As the hydrocarbon recovered is mainly the base oil of the drilling fluid, it could potentially be reused in future drilling operations.

4.2.5 Results Comparison to Previous Studies

Figure 4.16 highlights the extraction efficiency results from this study and compares them to extraction efficiencies from previous studies examining the removal of hydrocarbons from drilling waste using SC CO_2 [20-22]. Each diamond symbol for the current research is the average of the extraction efficiencies for each grouping of results from Table 4.3. The density of the fluid was determined using the *Thermophysical Properties of Fluid Systems* database provided by the National Institute of Standards and Technology (NIST) [105]. The results of the current research agree with the previous results showing extraction efficiencies and show efficiencies as high as 98.1%.

The general trend in the data suggests that as the density of the SC CO_2 increases (through a change in process pressure and temperature), the efficiency of the extraction increases. At densities greater than 0.55 $g{\cdot}mL^{-1}$, the increased density only slightly increases the extraction efficiency. No investigation was made into the effect of a change in SC CO_2 density in the current research.

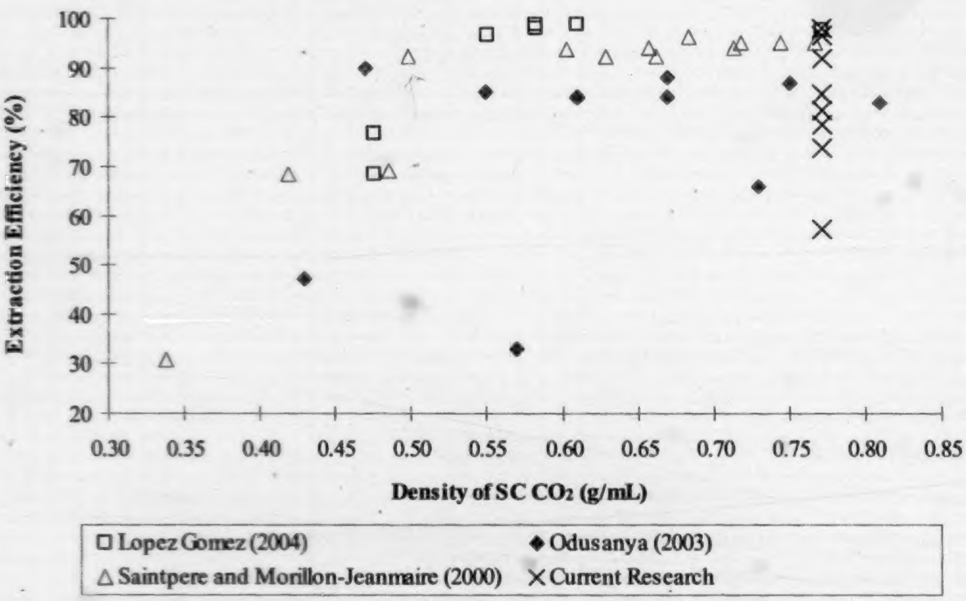


Figure 4.16 Comparison of extraction efficiencies from the current and previous studies of SFE of hydrocarbon based drilling wastes with SC CO_2

CHAPTER 5 - CONCLUSION AND RECOMMENDATIONS

The objectives of this research were to optimize the extraction of hydrocarbons from drilling waste by altering the process parameters of flow rate, mixing speed, vessel outlet design, initial waste mass, and waste texture using additives. Several studies have been completed, both at the University of Alberta and elsewhere, which have determined that the process can be optimized in terms of pressure and temperature (SC CO_2 density). This research, therefore attempted to apply already determined optimum conditions of pressure and temperature to a different waste sample to examine the ease of application of the technology from one waste type to another. In doing so, another goal of this research was to resolve process problems identified in previous studies to develop a more robust lab scale SFE setup that could be easily applied to various types of drilling wastes.

The starting point for the extractions in this research was the study completed in 2004 by Lopez Gomez using the same SFE setup. Within the study by Lopez Gomez, it was determined that 100 g of diesel-contaminated, centrifuge underflow drilling waste could be treated with 98% efficiency using SC CO_2 at 14.5 MPa and 40°C. Mixing was applied at 800 rpm using a ribbon blender. It quickly became apparent that a direct transfer of these determined optimum conditions was not possible: the first extraction runs completed using these exact conditions on the synthetic-contaminated, centrifuge underflow drilling waste were unable to be completed due to solids carryover and severe clogging of the downstream lines and valves.

Adjustments were made to the mass of waste treated and, more importantly, to the mixing speed. A reduction in the mixing speed from 800 rpm to 50 rpm allowed the SC CO_2 to contact the waste without forcing the waste against the lid of the vessel where it was more susceptible to clogging the outlet lines. Another advantage to reducing the mixing speed is a reduction in the power requirements of the system; not a major issue on a lab scale but would impact the economics when considering a pilot or commercial scale system.

Even with a reduction in mixing speed, the flow of SC CO_2 through the vessel resulted in some solids carryover. To prevent solids carryover, an outlet modification was developed: a 1 mm thick piece of Teflon® was placed at the top of the vessel as a physical boundary between the solids and the outlet. The Teflon® barrier would easily allow the hydrocarbon loaded SC CO_2 to pass, but would prevent the solids from reaching the outlet. The results were successful (i.e. no solids carryover) at SC CO_2 flow rates of 9.6 to 19.3 $g{\cdot}min^{-1}$ and 28.9 to 38.5 $g{\cdot}min^{-1}$. It should be noted here that an increase in SC CO_2 flow rate will increase the rate in which the hydrocarbons are removed from the waste. As SFE is a batch process, it is advantageous to complete each run as quickly as possible. The remainder of the runs completed in this research made use of the outlet modification and the higher flow rate.

While the results of these early tests were encouraging, they were not in the 98% efficiency range as reported by Lopez Gomez. To increase the contact between the SC CO_2 and the waste, several tests were conducted to determine the effect of using an additive. Both additives, A1 and A2, produced excellent results with extraction efficiencies of 98.1% and 96.8%, respectively. While less of A1 was required, concerns were expressed over whether or not the treated solids would be permitted to be released to the environment if they contained additive A1.

Further trials were conducted using a more "natural" additive, A2, in attempts to increase the mass of waste that could be treated. Again, increasing the mass of waste treated per run is advantageous due to the batch nature of SFE. It was determined that the maximum amount of solids that could be handled by the system without carryover and clogging was a total mass of approximately 150 g (waste and additive). However, the quantitative results for these runs were not as good with an average final treated hydrocarbon content of 1.0%. This concentration exceeds the limit for closure of a land treatment site in Alberta (0.5% in the topsoil layer).

The best results obtained for the full set of experiments completed during this research were completed on 50 g of waste plus A2 (for a total mass of approximately 65 g). The SC CO_2 flow rate, as measured at the pumps, was between 28.9 to 38.5 $g{\cdot}min^{-1}$ and the mixing speed was 50 rpm. These extraction conditions resulted in an average final hydrocarbon content of 0.4%. This concentration of hydrocarbons is below the regulated limit for release of synthetic contaminated drill cuttings to sea (6.9 g per 100 g of waste for offshore Canadian operations) and below the limit for site closure for land treatment in Alberta. More importantly, however, this research has resulted in improvements to the lab scale system that will allow the technology to be applied more broadly to different drilling waste samples and potentially applied more easily at a larger scale.

Finally, the results of this research agree with the previously published studies investigating the use of SC CO_2, although their main focus has been to optimize the process through investigating the effect of SC CO_2 density rather than other process parameters such as mixing speed, flow rate, additives, and vessel design. SC CO_2

densities above 0.55 g·mL^{-1} generally result in extraction efficiencies greater than 90%. In addition to efficiency, a few other studies have investigated the effect of the extraction on the quality of the hydrocarbon. They have visually confirmed (through GC/FID analysis) that the hydrocarbon is not changed by SFE. The fact that the hydrocarbon is unaltered by the process is important because the hydrocarbon is recovered, unlike other treatment technologies such as bioremediation. There is the potential for the recovered hydrocarbon to be reused in future drilling operations. The GC/FID analysis completed in this research corroborates this result.

In terms of future work, the improvements made to the lab scale system need to be tested on various drilling wastes. Also, it would be interesting to investigate the possibility of using other, more natural additives, like A2. This type of additive would lend itself well to the mobility of a field-scale SFE system (for example, a skid mounted system the travels to on-shore drill sites).

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APPENDICES

APPENDIX A - SAMPLE OUTPUT DATA FROM SFE SYSTEM

Date:04-03-06
Comments: cent undflo drill waste, no add, 50 g, 2100 psi, 40 deg, 30 min stat, 90 min dyn, begin stat at 1190 sec, begin dyn at 3030 sec, end extrn phase at 8570 sec

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A (mL·min^{-1})	Pump Flow B (mL·min^{-1})	Pump Pressure A (psi)	Pump Pressure B (psi)
0	10.55	104.75	30.08	0	0	810	801
1	20.16	97.97	30.31	0	0	809	800
2	30.98	100.28	30.48	0	0	809	800
3	40.59	105.23	30.59	0	0	808	799
4	50.15	107.87	30.70	0	0	808	799
5	60.97	100.63	30.88	0	0	808	799
6	70.58	103.24	30.99	0	0	807	798
7	80.14	96.28	31.22	0	0	807	798
8	90.96	119.69	31.28	0	0	807	798
9	100.57	128.60	31.34	0	0	807	798
10	110.18	116.76	31.51	0	0	809	801
11	120.95	136.23	31.57	0	0	808	800
12	130.56	141.37	31.75	0	0	808	800
13	140.17	113.94	31.86	0	0	808	799
14	150.94	108.46	31.98	0	0	808	799
15	160.55	84.54	32.10	0	0	808	799
16	170.27	96.17	32.16	0	0	811	802
17	181.04	93.12	32.40	0	0	815	806
18	190.65	119.52	32.40	0	0	816	807
19	200.26	112.44	32.57	0	0	815	806
20	211.03	107.20	32.63	0	0	814	805
21	220.64	101.29	32.75	0	0	814	805
22	230.25	102.06	32.81	0	0	814	805
23	241.02	107.68	32.93	0	0	814	805
24	250.63	101.44	33.00	0	0	813	804
25	260.24	116.06	33.06	0	0	813	804
26	271.01	120.42	33.18	0	0	813	804
27	280.62	106.41	33.24	0	0	813	804
28	290.23	111.88	33.30	0	0	813	804
29	301.05	90.21	33.48	0	0	813	804
30	310.61	112.51	33.60	0	0	812	803
31	320.22	107.45	33.54	0	0	812	803
32	331.04	109.48	33.67	0	0	812	803
33	340.60	108.24	33.79	0	0	811	802
34	350.21	119.05	33.85	0	0	811	802
35	361.03	98.51	33.85	0	0	810	801
36	370.64	98.53	34.04	0	0	810	801
37	380.20	121.03	34.16	0	0	810	801
38	391.02	110.16	34.29	0	0	809	800
39	400.63	113.76	34.29	0	0	809	800

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A (mL·min^{-1})	Pump Flow B (mL·min^{-1})	Pump Pressure A (psi)	Pump Pressure B (psi)
40	410.19	101.24	34.41	0	0	809	800
41	421.01	104.49	34.48	0	0	808	800
42	430.62	106.79	34.66	0	0	810	801
43	440.23	102.58	34.73	0	0	810	801
44	451.00	101.22	34.85	0	0	809	800
45	460.61	121.23	34.85	0	0	809	800
46	470.28	111.30	34.98	0	0	808	799
47	481.10	104.22	35.05	0	0	808	799
48	490.71	110.84	35.11	0	0	808	799
49	500.32	109.48	35.24	0	0	808	799
50	511.09	105.78	35.24	0	0	807	798
51	520.70	125.32	35.30	0	0	807	798
52	530.31	115.12	35.37	0	0	807	798
53	541.07	94.80	35.43	0	0	806	798
54	550.69	106.86	35.37	0	0	806	797
55	560.30	110.71	35.49	0	0	806	797
56	571.06	120.85	35.62	0	0	806	797
57	580.68	106.32	35.69	0	0	805	797
58	590.29	108.93	35.88	0	0	805	796
59	601.11	108.82	35.82	0	0	805	796
60	610.66	107.49	35.82	0	0	805	796
61	620.28	107.05	35.95	0	0	804	795
62	631.10	102.73	35.95	0	0	804	795
63	640.65	109.80	35.95	0	0	804	795
64	650.27	92.94	36.08	0	0	803	794
65	661.09	113.92	36.21	0	0	803	794
66	670.70	121.49	36.21	0	0	803	794
67	680.26	117.69	36.28	0	0	803	794
68	691.08	99.26	36.34	0	0	802	793
69	700.69	106.96	36.48	0	0	802	793
70	710.24	107.01	36.48	0	0	802	793
71	721.07	95.92	36.61	0	0	802	793
72	730.68	106.26	36.61	0	0	801	793
73	740.29	106.46	36.61	0	0	801	793
74	751.05	114.99	36.74	0	0	802	793
75	760.67	116.82	36.74	0	0	803	794
76	770.33	97.73	36.68	0	0	804	795
77	781.15	110.58	36.88	0	0	804	795
78	790.77	106.07	36.94	0	0	804	795
79	800.38	105.48	37.08	0	0	804	795
80	811.14	99.23	37.15	0	0	799	789
81	820.75	96.59	37.28	0	0	797	789
82	830.37	129.64	37.35	0	0	797	789
Refilling pumps							
83	841.13	114.65	37.35	-203.61	-203.58	791	782
84	850.74	103.27	37.42	-204.08	-204.03	780	772
85	860.36	99.04	37.49	-204.07	-204.04	770	763

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A (mL·min^{-1})	Pump Flow B (mL·min^{-1})	Pump Pressure A (psi)	Pump Pressure B (psi)
86	871.12	106.39	37.55	-204.07	-204.080	768	761
87	880.73	102.45	37.55	-204.131	-204.093	766	759
88	890.35	114.67	37.62	-204.15	-204.070	765	758
89	901.11	97.37	37.62	-203.979	-204.07	763	756
90	910.72	100.25	37.62	0	-204.08	775	766
91	920.33	118.80	37.69	0	-204.080	777	767
92	931.16	113.80	37.76	0	0	786	778
93	940.71	103.97	37.69	0	0	787	779
94	950.32	106.45	37.76	0	0	788	779
95	961.14	96.80	37.76	0	0	788	780
Running pumps							
96	970.70	105.29	37.83	0	0	788	780
97	980.31	96.24	37.83	0	197.18201	789	815
98	991.13	99.54	37.76	195.679	195.972	918	998
99	1000.75	110.08	37.83	194.138	147.772	1157	1579
100	1010.30	124.86	37.83	60.719	33.723	1887	1976
101	1021.12	110.84	37.83	25.755	13.745	2080	2100
102	1030.74	116.95	37.83	13.52	10.213	2100	2100
103	1040.29	107.49	37.90	28.327	41.768	2083	2058
104	1051.11	934.32	41.76	71.823	96.886	2052	2010
105	1060.72	1032.71	42.47	29.355	115.521	2114	2072
106	1070.34	1167.44	41.61	4.751	140.808	2093	2100
107	1081.10	1254.64	39.09	3.513	131.614	2100	2100
108	1090.71	1316.51	36.94	3.267	126.527	2100	2100
109	1100.33	1361.82	37.21	2.962	121.774	2100	2100
110	1111.09	1432.19	38.67	2.698	117.234	2100	2100
111	1120.70	1466.89	40.03	2.494	113.227	2100	2100
112	1130.32	1527.66	41.23	2.332	109.931	2100	2100
113	1141.08	1586.04	42.39	2.159	104.661	2100	2100
114	1150.69	1650.13	43.27	2.001	98.99	2100	2100
115	1160.30	1806.26	45.01	1.904	83.061	2100	2100
116	1171.07	1975.75	46.58	1.755	62.789	2100	2100
Begin 15 minute static phase							
117	1180.68	2100.07	47.03	1.697	43.949	2100	2100
118	1190.29	2161.89	47.03	1.598	26.885	2100	2100
119	1201.11	2210.58	46.40	1.514	15.568	2100	2100
120	1210.67	2216.79	46.04	1.44	10.933	2100	2100
121	1220.28	2210.39	45.44	1.349	8.314	2100	2100
122	1231.10	2215.71	45.01	1.291	7.152	2100	2100
123	1240.66	2213.69	44.67	1.242	6.227	2100	2100
124	1250.27	2220.82	44.42	1.202	5.271	2100	2100
125	1261.09	2234.84	44.17	1.123	3.824	2100	2100
126	1270.70	2231.13	43.92	1.085	4.273	2100	2100
127	1280.26	2237.33	43.75	1.038	4.928	2100	2100
128	1291.08	2234.96	43.67	0.998	4.623	2100	2100
129	1300.69	2231.02	43.67	0.942	4.553	2100	2100
130	1310.25	2245.37	43.59	0.913	2.998	2100	2100

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A (mL·min^{-1})	Pump Flow B (mL·min^{-1})	Pump Pressure A (psi)	Pump Pressure B (psi)
131	1321.07	2240.82	43.51	0.882	2.755	2100	2100
132	1330.68	2225.76	43.43	0.832	2.589	2100	2100
133	1340.30	2233.70	43.43	0.795	2.165	2100	2100
134	1351.06	2236.92	43.18	0.763	1.992	2100	2100
135	1360.67	2231.65	43.18	0.739	1.967	2100	2100
136	1370.28	2232.74	43.35	0.696	1.966	2100	2100
137	1381.05	2222.46	43.10	0.666	1.882	2100	2100
138	1390.66	2249.59	43.27	0.651	1.572	2100	2100
139	1400.27	2241.81	43.18	0.617	1.143	2100	2100
140	1411.04	2225.89	43.35	0.599	1.361	2100	2100
141	1420.65	2224.79	43.27	0.557	1.197	2100	2100
142	1430.26	2231.21	43.18	0.631	1.519	2100	2100
143	1441.08	2226.75	43.27	0.531	1.113	2100	2100
144	1450.64	2237.05	43.27	0.478	1.137	2100	2100
145	1460.25	2234.66	43.18	0.477	1.346	2100	2100
146	1471.07	2222.50	43.10	0.46	0.912	2100	2100
147	1480.63	2248.01	43.10	0.445	0.972	2100	2100
148	1490.24	2231.10	43.35	0.423	1.307	2100	2100
149	1501.06	2200.94	43.18	0.414	1.06	2100	2100
150	1510.62	2218.13	43.27	0.379	0.52	2100	2100
151	1520.23	2238.19	43.27	0.365	0.98	2100	2100
152	1531.05	2230.87	43.27	0.359	1.138	2100	2100
153	1540.66	2228.26	43.35	0.345	1.112	2100	2100
154	1550.22	2233.23	43.27	0.348	0.817	2100	2100
155	1561.04	2224.67	43.35	0.331	0.894	2100	2100
156	1570.65	2227.56	43.27	0.323	0.917	2100	2100
157	1580.21	2226.52	43.27	0.302	0.733	2100	2100
158	1591.03	2219.19	43.35	0.293	0.816	2100	2100
159	1600.64	2232.60	43.43	0.297	0.961	2100	2100
160	1610.25	2225.95	43.27	0.219	0.604	2100	2100
161	1621.02	2228.58	43.35	0.26	0.745	2100	2100
162	1630.63	2233.32	43.35	0.27	0.986	2100	2100
163	1640.24	2229.54	43.43	0.213	0.905	2100	2100
164	1651.01	2223.98	43.35	0.228	0.942	2100	2100
165	1660.62	2226.78	43.35	0.219	0.922	2100	2100
166	1670.34	2211.94	43.35	0.2	1.205	2100	2100
167	1681.11	2237.77	43.35	0.193	0.941	2100	2100
168	1690.72	2221.07	43.43	0.185	0.953	2100	2100
169	1700.33	2235.54	43.43	0.176	0.679	2100	2100
170	1711.10	2237.72	43.43	0.17	1.151	2100	2100
171	1720.71	2234.08	43.43	0.166	0.594	2100	2100
172	1730.32	2224.03	43.35	0.162	0.973	2100	2100
173	1741.09	2226.65	43.35	0.147	0.536	2100	2100
174	1750.70	2228.82	43.43	0.141	0.597	2100	2100
175	1760.31	2218.30	43.43	0.129	0.941	2100	2100
176	1771.13	2232.35	43.51	0.136	0.618	2100	2100
177	1780.69	2233.24	43.59	0.122	0.719	2100	2100

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A (mL·min^{-1})	Pump Flow B (mL·min^{-1})	Pump Pressure A (psi)	Pump Pressure B (psi)
178	1790.30	2233.73	43.43	0.114	0.831	2100	2100
179	1801.12	2235.62	43.43	0.108	0.755	2100	2100
180	1810.68	2235.50	43.51	0.111	0.456	2100	2100
181	1820.29	2256.94	43.43	0.11	0.729	2100	2100
182	1831.11	2246.48	43.51	0.095	0.784	2100	2100
183	1840.72	2220.81	43.35	0.091	0.525	2100	2100
184	1850.28	2235.89	43.51	0.1	0.674	2100	2100
185	1861.10	2227.37	43.43	0.097	0.334	2100	2100
186	1870.71	2242.85	43.59	0.058	0.781	2100	2100
187	1880.27	2240.36	43.43	0.082	0.717	2100	2100
188	1891.09	2222.09	43.43	0.078	0.407	2100	2100
189	1900.70	2223.88	43.43	0.062	0.652	2100	2100
190	1910.31	2228.85	43.43	0.055	0.753	2100	2100
191	1921.08	2239.67	43.51	0.065	0.696	2100	2100
192	1930.69	2225.29	43.51	0.06	0.686	2100	2100
193	1940.30	2266.00	43.35	0.054	0.485	2100	2100
194	1951.07	2237.96	43.51	0.057	0.466	2100	2100
195	1960.68	2217.69	43.51	0.062	0.587	2100	2100
196	1970.29	2214.59	43.43	0.053	0.51	2100	2100
197	1981.06	2236.61	43.43	0.033	0.359	2100	2100
198	1990.67	2236.52	43.43	0.031	0.88	2100	2100
199	2000.28	2219.36	43.43	0.029	0.566	2100	2100
200	2011.05	2249.19	43.43	0.045	0.533	2100	2100
201	2020.66	2229.67	43.51	0.051	0.616	2100	2100
202	2030.27	2243.51	43.35	0.06	0.574	2100	2100
203	2041.09	2219.87	43.59	0.042	0.364	2100	2100
204	2050.65	2223.18	43.51	0.032	0.425	2100	2100
205	2060.26	2223.53	43.43	0.022	0.715	2100	2100
206	2071.08	2241.67	43.43	0.023	0.816	2100	2100
207	2080.64	2227.68	43.43	0.016	0.671	2100	2100
208	2090.25	2232.70	43.35	0.028	0.44	2100	2100
209	2101.07	2236.00	43.35	0.03	0.584	2100	2100
210	2110.68	2239.72	43.43	0.055	0.422	2100	2100
211	2120.24	2247.88	43.43	0.021	0.689	2100	2100
212	2131.06	2226.02	43.43	0.014	0.629	2100	2100
213	2140.67	2234.60	43.43	0.026	0.534	2100	2100
214	2150.23	2209.16	43.35	0.032	0.601	2100	2100
215	2161.05	2242.97	43.43	0.012	0.634	2100	2100
216	2170.66	2221.07	43.35	0.024	0.689	2100	2100
217	2180.27	2216.19	43.35	0.03	0.464	2100	2100
218	2191.04	2233.90	43.35	0.003	0.868	2100	2100
219	2200.65	2231.79	43.35	0.032	0.424	2100	2100
220	2210.26	2224.89	43.59	0.002	0.428	2100	2100
221	2221.03	2211.09	43.35	0.021	0.741	2100	2100
222	2230.64	2238.52	43.35	0.019	0.375	2100	2100
223	2240.25	2228.60	43.27	0.02	0.543	2100	2100
224	2251.01	2218.13	43.43	0.021	0.63	2100	2100

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A (mL·min^{-1})	Pump Flow B (mL·min^{-1})	Pump Pressure A (psi)	Pump Pressure B (psi)
225	2260.63	2248.40	43.27	0.016	0.663	2100	2100
226	2270.35	2226.14	43.27	0.012	0.461	2100	2100
227	2281.11	2231.69	43.35	0.011	0.599	2100	2100
228	2290.73	2239.75	43.27	0.003	0.729	2100	2100
229	2300.34	2247.60	43.35	0.038	0.497	2100	2100
230	2311.10	2231.84	43.35	0	0.388	2100	2100
231	2320.72	2240.27	43.18	0.035	0.389	2100	2100
232	2330.33	2222.71	43.27	0.006	0.566	2100	2100
233	2341.09	2235.86	43.35	0.004	0.647	2100	2100
234	2350.70	2236.22	43.27	0.033	0.508	2100	2100
235	2360.32	2232.74	43.18	0.002	0.464	2100	2100
236	2371.14	2230.21	43.18	0.028	0.638	2100	2100
237	2380.69	2246.87	43.18	0.005	0.632	2100	2100
238	2390.31	2223.11	43.27	0.024	0.658	2100	2100
239	2401.13	2219.60	43.18	0.008	0.497	2100	2100
240	2410.68	2238.13	43.27	0.025	0.591	2100	2100
241	2420.30	2231.81	43.18	0.009	0.712	2100	2100
242	2431.12	2238.78	43.10	0.013	0.341	2100	2100
243	2440.73	2237.64	43.18	0.042	0.559	2100	2100
244	2450.28	2226.55	43.10	0.002	0.666	2100	2100
245	2461.10	2234.34	43.10	0.026	0.158	2100	2100
246	2470.72	2232.33	43.10	0.037	0.653	2100	2100
247	2480.38	2237.65	43.10	0.017	0.563	2100	2100
248	2490.00	2223.46	43.10	0.015	0.535	2100	2100
249	2500.82	2232.83	43.10	0.04	0.63	2100	2100
250	2510.37	2250.16	43.02	0.028	0.737	2100	2100
251	2521.19	2239.13	43.02	0.004	1.173	2100	2100
252	2530.81	2234.78	43.02	0.031	1.528	2100	2100
253	2540.42	2230.49	43.10	0.031	1.47	2100	2100
254	2551.18	2231.81	43.10	0.006	1.446	2100	2100
255	2560.79	2234.84	43.02	0.025	1.452	2100	2100
256	2570.46	2233.67	42.94	0.043	1.347	2100	2100
257	2580.07	2248.73	42.94	0.014	1.521	2100	2100
258	2590.89	2234.55	42.94	0.01	1.688	2100	2100
259	2600.51	2250.12	43.02	0.033	1.662	2100	2100
260	2610.06	2237.58	43.02	0.003	1.463	2100	2100
261	2620.88	2232.01	43.02	0.037	1.635	2100	2100
262	2630.50	2246.65	42.86	0.024	1.712	2100	2100
263	2640.05	2222.48	43.02	0.01	1.418	2100	2100
264	2650.87	2251.60	42.86	0.032	1.606	2100	2100
265	2660.48	2239.51	42.94	0.022	1.717	2100	2100
266	2670.10	2218.59	43.02	0.012	1.559	2100	2100
267	2680.86	2236.30	42.86	0.022	1.567	2100	2100
268	2690.47	2225.60	42.86	0.009	1.781	2100	2100
269	2700.09	2247.32	42.86	0	1.731	2100	2100
270	2710.85	2249.77	42.86	0.019	1.709	2100	2100
271	2720.46	2233.55	42.86	0.024	1.671	2100	2100

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A ($mL{\cdot}min^{-1}$)	Pump Flow B ($mL{\cdot}min^{-1}$)	Pump Pressure A (psi)	Pump Pressure B (psi)
272	2730.07	2255.33	42.94	0	1.762	2100	2100
273	2740.84	2236.80	42.78	0	1.615	2100	2100
274	2750.45	2225.05	42.78	0.006	1.799	2100	2100
275	2760.06	2240.23	42.86	0.015	1.72	2100	2100
276	2770.83	2226.78	42.86	0.018	1.854	2100	2100
277	2780.44	2230.65	42.78	0	1.806	2100	2100
278	2790.05	2229.30	42.78	0	1.614	2100	2100
279	2800.87	2248.54	42.78	0	1.723	2100	2100
280	2810.43	2216.54	42.70	0	1.676	2100	2100
281	2820.04	2223.34	42.70	0	2.116	2100	2100
282	2830.86	2241.96	42.70	0	1.829	2100	2100
283	2840.42	2239.07	42.70	0	1.848	2100	2100
284	2850.03	2211.06	42.70	0	1.843	2100	2100
285	2860.85	2232.26	42.70	0	1.679	2100	2100
286	2870.52	2226.28	42.63	0	1.686	2100	2100
287	2880.13	2231.40	42.63	0	1.713	2100	2100
288	2890.95	2224.13	42.63	0	1.7	2100	2100
289	2900.56	2230.06	42.63	0.001	1.781	2100	2100
290	2910.12	2229.95	42.70	0.004	1.737	2100	2100
291	2920.94	2252.48	42.63	0	1.838	2100	2100
292	2930.55	2223.49	42.63	0	1.717	2100	2100
293	2940.11	2220.13	42.63	0	1.713	2100	2100
294	2950.93	2232.41	42.55	0	1.863	2100	2100
295	2960.65	2236.07	42.55	0	1.737	2100	2100
296	2970.21	2214.86	42.55	0	1.893	2100	2100
297	2981.03	2226.11	42.63	0	1.751	2100	2100
298	2990.64	2234.55	42.47	0	2.074	2100	2100
			Begin 90 minute dynamic phase				
299	3000.31	2207.68	42.23	0.052	23.456	2100	2100
300	3011.13	2220.75	42.08	0	17.387	2100	2100
301	3020.74	2222.99	42.15	0	16.446	2100	2100
302	3030.30	2211.62	42.08	0	15.888	2100	2100
303	3041.12	2219.53	42.08	0	15.428	2100	2100
304	3050.73	2221.52	42.00	0	16.164	2100	2100
305	3060.29	2212.84	42.00	0	15.329	2100	2100
306	3071.11	2223.34	41.92	0	14.941	2100	2100
307	3080.72	2201.82	42.00	0	15.14	2100	2100
308	3090.33	2206.14	42.00	0	14.973	2100	2100
309	3101.10	2219.84	42.08	0	14.759	2100	2100
310	3110.71	2207.14	41.92	0	14.245	2100	2100
311	3120.32	2175.07	41.69	0	29.324	2100	2085
312	3131.09	2191.58	41.61	0	24.274	2100	2100
313	3140.70	2215.21	41.92	0	15.084	2100	2067
314	3150.31	2186.57	41.53	0	29.495	2100	2100
315	3161.08	2248.59	41.76	0	-1.259	2100	2108
316	3170.80	2179.28	41.84	0	27.345	2100	2085
317	3180.41	2238.84	41.69	0	10.381	2100	2110

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A (mL·min^{-1})	Pump Flow B (mL·min^{-1})	Pump Pressure A (psi)	Pump Pressure B (psi)
318	3191.17	2206.36	41.76	0	19.308	2100	2081
319	3200.79	2206.68	41.69	0	19.015	2100	2100
320	3210.40	2209.47	41.76	0	18.567	2100	2100
321	3220.01	2224.15	41.84	0	5.635	2100	2111
322	3230.78	2202.16	41.76	0	18.821	2100	2091
323	3240.50	2206.99	41.69	0	18.132	2100	2100
324	3250.11	2190.56	41.69	0	17.044	2100	2100
325	3260.87	2185.46	41.84	0	14.532	2100	2081
326	3270.49	2219.78	41.69	0	17.337	2100	2100
327	3280.10	2202.63	41.76	0	16.675	2100	2079
328	3290.86	2223.13	41.53	0	17.482	2100	2100
329	3300.48	2240.80	41.76	0	-0.205	2100	2093
330	3310.09	2192.97	41.61	0	21.234	2100	2100
331	3320.85	2217.70	41.61	0	18.177	2100	2100
332	3330.47	2229.68	41.53	0	17.383	2100	2100
333	3340.08	2245.91	41.69	0	-0.19	2100	2100
334	3350.84	2197.57	41.53	0	18.68	2100	2100
335	3360.45	2216.78	41.53	0	15.797	2100	2100
336	3370.07	2208.90	41.53	0	16.167	2100	2100
337	3380.89	2229.74	41.53	0	8.706	2100	2107
338	3390.44	2195.76	41.61	-0.019	14.152	2100	2079
339	3400.06	2216.72	41.38	0	17.116	2100	2100
340	3410.88	2217.99	41.46	0	11.907	2100	2107
341	3420.43	2195.54	41.46	-0.012	17.82	2100	2090
342	3430.05	2234.72	41.46	0	6.743	2100	2108
343	3440.87	2207.74	41.46	-0.013	17.204	2100	2089
344	3450.48	2204.08	41.46	-0.016	15.347	2100	2100
345	3460.03	2229.54	41.46	-0.089	11.949	2100	2106
346	3470.86	2238.06	41.38	-0.026	16.61	2100	2088
347	3480.47	2181.17	41.23	10.426	0	2081	2044
Refill pump B, run pump A							
348	3490.02	2203.15	41.15	-1.107	-204.013	2100	774
349	3500.95	2207.87	41.23	0.053	-204.05499	2100	777
350	3510.57	2148.06	41.08	17.139	-203.884	2100	772
351	3520.12	2171.22	41.23	12.415	-204.08501	2088	773
352	3530.94	2187.71	41.00	10.716	-203.731	2108	773
353	3540.56	2139.99	41.08	24.37	-204.043	2069	774
354	3550.11	2147.89	40.78	20.91	-204.05499	2068	774
355	3560.93	2139.96	40.93	18.981	-204.07401	2106	774
356	3570.54	2165.80	41.15	10.461	-204.07401	2072	774
357	3580.16	2183.95	41.00	18.121	-204.089	2110	774
358	3590.92	2160.41	40.93	25.34	-204	2087	774
359	3600.53	2191.99	41.08	9.068	-204.104	2108	774
360	3610.15	2122.21	40.93	28.377	-204.07401	2083	774
361	3620.91	2183.32	41.08	16.997	-204.142	2084	773
362	3630.52	2192.15	41.00	8.642	0	2116	778
Run pump B							

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A ($mL \cdot min^{-1}$)	Pump Flow B ($mL \cdot min^{-1}$)	Pump Pressure A (psi)	Pump Pressure B (psi)
363	3640.14	2127.13	41.00	27.806	197.673	2081	808
364	3650.90	2173.92	40.85	21.984	196.056	2100	954
365	3660.51	2195.79	41.08	-2.013	194.077	2105	1194
366	3670.12	2138.85	40.85	30.588	66.522	2089	1859
367	3680.95	2174.81	40.93	20.374	30.382	2100	2052
368	3690.50	2185.47	41.08	-0.599	35.523	2100	2082
369	3700.11	2231.24	41.08	-0.414	15.393	2100	2116
370	3710.93	2193.00	40.85	-2.207	37.753	2105	2091
371	3720.49	2188.87	40.93	0.369	30.317	2100	2100
372	3730.10	2190.83	41.00	-0.53	30.786	2100	2100
373	3740.92	2184.30	40.85	-0.802	30.454	2100	2100
374	3750.48	2181.56	40.85	-0.194	28.186	2100	2100
375	3760.09	2193.78	40.78	-0.181	28.498	2100	2100
376	3770.91	2222.26	41.00	-0.147	1.225	2100	2100
377	3780.52	2182.16	40.70	-1.56	30.515	2100	2087
378	3790.08	2183.69	40.70	0.376	25.443	2100	2100
379	3800.90	2193.49	40.78	-0.041	24.716	2100	2100
380	3810.51	2232.51	40.85	-0.05	17.645	2100	2100
381	3820.07	2131.85	40.55	0.001	33.723	2100	2100
382	3830.89	2179.70	40.78	-0.051	24.354	2100	2100
383	3840.50	2190.07	40.70	-0.098	26.972	2100	2094
384	3850.12	2178.54	40.70	-0.032	28.34	2100	2100
385	3860.88	2158.74	40.70	-0.07	24.448	2100	2100
386	3870.49	2196.65	40.70	-0.028	22.642	2100	2100
387	3880.10	2194.28	40.63	-0.136	29.846	2100	2100
388	3890.87	2149.94	40.55	-0.048	27.292	2100	2100
389	3900.48	2166.97	40.63	-0.027	27.606	2100	2100
390	3910.09	2184.99	40.55	-0.022	27	2100	2100
391	3920.86	2162.81	40.55	-0.091	25.639	2100	2100
392	3930.47	2191.52	40.55	-0.1	20.91	2100	2100
393	3940.08	2211.28	40.70	-0.09	16.797	2100	2100
394	3950.90	2234.81	40.78	-0.079	3.12	2100	2088
395	3960.46	2187.06	40.63	0	21.801	2100	2093
396	3970.07	2219.27	40.63	-0.054	-0.007	2100	2100
397	3980.89	2188.95	40.63	0.072	17.303	2100	2079
398	3990.45	2256.15	40.63	0.016	-1.784	2100	2100
399	4000.06	2162.20	40.48	-0.544	29.058	2100	2081
400	4010.88	2162.52	40.33	3.984	15.549	2085	2063
401	4020.44	2156.81	40.25	-0.243	30.508	2100	2092
402	4030.05	2184.57	40.33	0.179	27.992	2100	2100
403	4040.87	2224.35	40.40	0.024	10.388	2100	2100
404	4050.48	2176.71	40.40	0	25.8	2100	2084
405	4060.04	2200.65	40.40	-0.014	18.947	2100	2083
406	4070.86	2175.62	40.25	0	30.607	2100	2082
407	4080.47	2156.34	40.11	0	31.63	2100	2100
408	4090.03	2181.59	40.18	0	27.509	2100	2100
409	4100.85	2181.93	40.25	0	24.894	2100	2100

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A ($\mathrm{mL \cdot min^{-1}}$)	Pump Flow B ($\mathrm{mL \cdot min^{-1}}$)	Pump Pressure A (psi)	Pump Pressure B (psi)
410	4110.57	2237.93	40.40	0	6.347	2100	2106
411	4120.13	2217.33	40.40	-1.107	15.447	2100	2090
412	4130.95	2193.97	40.25	-0.001	24.244	2100	2100
413	4140.56	2209.73	40.33	0	13.14	2100	2105
414	4150.17	2205.62	40.48	0	1.472	2100	2100
415	4160.94	2232.07	40.48	0	1.608	2100	2100
416	4170.55	2168.29	40.18	-1.084	29.214	2100	2089
417	4180.16	2185.56	40.03	-0.018	27.65	2100	2100
418	4190.93	2174.97	40.03	0	27.034	2100	2100
419	4200.54	2188.71	40.25	0	27.302	2100	2100
420	4210.15	2206.66	40.03	0	26.549	2100	2100
421	4220.92	2182.72	40.11	0	27.09	2100	2100
422	4230.53	2193.82	39.96	0	28.449	2100	2100
423	4240.14	2158.65	39.89	-0.036	28.263	2100	2100
424	4250.91	2205.01	40.03	-0.029	27.128	2100	2100
425	4260.52	2178.33	40.03	-0.026	25.498	2100	2100
426	4270.13	2179.32	40.03	-0.028	24.524	2100	2100
427	4280.95	2189.02	40.11	-0.022	22.554	2100	2100
428	4290.51	2194.42	40.03	-0.063	22.392	2100	2100
429	4300.12	2208.05	40.03	-0.081	22.648	2100	2100
430	4310.94	2208.00	40.11	-0.051	18.232	2100	2100
431	4320.50	2203.49	40.18	-0.066	18.007	2100	2100
432	4330.11	2210.58	40.03	-0.071	17.686	2100	2100
433	4340.93	2198.75	39.96	-0.036	17.664	2100	2100
434	4350.54	2254.82	40.03	-0.032	17.579	2100	2100
435	4360.10	2208.34	39.96	-0.016	17.445	2100	2100
436	4370.92	2220.64	39.96	-0.033	17.613	2100	2100
437	4380.53	2224.80	39.89	-0.027	17.905	2100	2100
438	4390.09	2196.83	39.81	-0.009	17.453	2100	2100
439	4400.91	2214.21	39.89	-0.017	17.468	2100	2100
440	4410.52	2213.29	39.89	0	18.028	2100	2100
441	4420.13	2170.80	39.74	0	20.693	2100	2100
442	4430.90	2210.74	39.74	0	17.947	2100	2100
443	4440.51	2186.65	39.89	0	17.6	2100	2100
444	4450.12	2257.43	39.74	0	17.614	2100	2100
445	4460.89	2189.58	39.81	0	16.732	2100	2100
446	4470.50	2245.62	39.74	0	16.876	2100	2100
447	4480.11	2173.95	39.74	0	17.541	2100	2100
448	4490.88	2242.37	39.60	0	16.724	2100	2100
449	4500.49	2216.46	39.67	0	17.211	2100	2100
450	4510.10	2202.52	39.67	0	17.329	2100	2100
451	4520.87	2197.22	39.60	-0.042	17.503	2100	2100
452	4530.48	2250.10	39.67	0	17.152	2100	2100
453	4540.09	2241.72	39.60	0	17.09	2100	2100
454	4550.91	2202.86	39.74	0	17.234	2100	2100
455	4560.47	2212.32	39.67	0	17.071	2100	2100
456	4570.08	2200.90	39.60	0	16.848	2100	2100

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A (mL·min^{-1})	Pump Flow B (mL·min^{-1})	Pump Pressure A (psi)	Pump Pressure B (psi)
457	4580.90	2239.07	39.60	-0.032	16.815	2100	2100
458	4590.46	2208.69	39.52	-0.009	16.89	2100	2100
459	4600.07	2199.77	39.45	0	16.791	2100	2100
460	4610.89	2200.61	39.52	0	16.691	2100	2100
461	4620.50	2192.24	39.45	0	16.793	2100	2100
462	4630.06	2241.97	39.52	0	16.699	2100	2100
463	4640.88	2254.04	39.45	0	16.434	2100	2100
464	4650.49	2208.43	39.52	-0.048	16.473	2100	2100
465	4660.05	2186.89	39.45	-0.025	16.533	2100	2100
466	4670.87	2212.28	39.31	0	16.685	2100	2100
467	4680.48	2245.36	39.31	0	16.509	2100	2100
468	4690.09	2263.78	39.45	0	16.487	2100	2100
469	4700.86	2175.13	39.31	0	16.422	2100	2100
470	4710.47	2192.14	39.38	-0.033	15.84	2100	2100
471	4720.08	2257.88	39.31	0	16.765	2100	2100
472	4730.85	2211.56	39.24	0	16.461	2100	2100
473	4740.46	2275.78	39.31	0	16.495	2100	2100
474	4750.07	2243.13	39.31	0	16.669	2100	2100
475	4760.84	2257.92	39.24	-0.029	16.676	2100	2100
476	4770.45	2209.66	39.24	0	16.657	2100	2100
477	4780.06	2254.50	39.24	0	16.553	2100	2100
478	4790.82	2213.73	39.16	0	16.3	2100	2100
479	4800.44	2207.02	39.24	-0.019	16.979	2100	2083
480	4810.05	2215.99	39.09	0	17.116	2100	2100
481	4820.87	2241.06	39.16	-0.038	16.502	2100	2100
482	4830.43	2206.23	39.16	0	16.423	2100	2100
483	4840.04	2228.22	39.09	0	16.442	2100	2100
484	4850.86	2219.47	39.16	0	16.383	2100	2100
485	4860.42	2230.83	39.09	0	16.583	2100	2100
486	4870.03	2202.86	39.16	-0.023	16.054	2100	2100
487	4880.85	2204.21	39.09	-0.004	15.939	2100	2100
488	4890.46	2228.17	39.09	0	16.754	2100	2100
Refill pump B, run pump A							
489	4900.02	2139.36	38.81	16.85	0	2081	2050
490	4910.84	2189.47	38.81	16.093	0	2100	2069
491	4920.45	2184.08	38.88	16.596	0	2100	2067
492	4930.01	2196.64	38.88	16.464	0	2100	2067
493	4940.83	2178.85	38.88	16.317	0	2100	2067
494	4950.44	2187.69	38.95	16.261	0	2100	2067
495	4960.05	2160.85	38.95	16.448	0	2100	2067
496	4970.82	2200.06	38.95	16.352	0	2100	2067
497	4980.43	2170.81	38.81	16.517	0	2100	2067
498	4990.04	2189.12	38.95	16.063	-204.028	2100	775
499	5000.80	2192.26	38.95	15.967	-204.047	2100	779
500	5010.42	2187.66	38.88	16.065	-204.097	2100	779
501	5020.03	2180.48	38.95	16.149	-203.56799	2100	774
502	5030.79	2151.36	38.95	16.086	-204.05099	2100	775

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A (mL·min^{-1})	Pump Flow B (mL·min^{-1})	Pump Pressure A (psi)	Pump Pressure B (psi)
503	5040.41	2189.30	38.95	16.259	-203.56799	2100	776
504	5050.02	2195.79	38.95	15.803	-204.062	2100	776
505	5060.78	2164.56	38.95	15.875	-203.56	2100	776
506	5070.40	2185.59	38.95	15.884	-204.03999	2100	776
507	5080.01	2185.75	38.88	16.151	-204.043	2100	776
508	5090.83	2191.73	38.95	16.252	-204.104	2100	776
509	5100.38	2189.96	38.95	16.158	-204.101	2100	776
510	5110.00	2196.42	38.88	15.746	-204.127	2100	775
511	5120.82	2216.29	38.88	15.714	-204.07401	2100	775
512	5130.37	2157.85	38.95	15.652	-204.097	2100	775
513	5141.19	2203.61	38.95	16.062	197.407	2100	836
514	5150.81	2157.04	38.88	16.019	196.39799	2100	940
				Run pump B			
515	5160.42	2201.56	38.95	15.727	195.028	2100	1095
516	5171.18	2150.71	39.02	15.449	81.474	2100	1811
517	5180.80	2192.30	38.88	15.503	33.712	2100	2014
518	5190.41	2206.11	38.95	-1.286	34.146	2100	2087
519	5201.17	2204.59	39.02	-0.496	29.891	2100	2100
520	5210.78	2211.43	38.95	-0.293	26.778	2100	2100
521	5220.40	2202.79	38.95	-0.134	24.354	2100	2100
522	5230.01	2217.16	38.88	-0.195	23.154	2100	2100
523	5240.77	2199.20	38.95	-0.185	22.026	2100	2100
524	5250.39	2197.51	38.88	-0.176	21.806	2100	2100
525	5260.00	2200.52	38.88	-0.757	21.32	2100	2100
526	5270.76	2165.96	38.95	-0.105	20.739	2100	2100
527	5280.38	2207.97	38.88	-0.112	19.95	2100	2100
528	5291.20	2211.64	38.88	-0.183	19.198	2100	2100
529	5300.75	2206.19	38.88	-0.075	19.339	2100	2100
530	5310.36	2225.38	38.88	-0.108	18.974	2100	2100
531	5321.19	2202.95	38.88	-0.654	18.822	2100	2100
532	5330.74	2213.39	38.88	-0.106	18.042	2100	2100
533	5340.35	2209.91	38.95	-0.076	17.422	2100	2100
534	5351.17	2200.80	39.02	-0.054	17.1	2100	2100
535	5360.79	2198.35	39.02	-0.056	17.282	2100	2100
536	5370.34	2211.25	39.16	-0.046	17.077	2100	2100
537	5381.16	2196.31	39.09	-0.051	16.748	2100	2100
538	5390.78	2215.36	39.16	-0.092	16.932	2100	2100
539	5400.33	2209.20	39.16	-0.133	16.551	2100	2100
540	5411.15	2224.83	39.24	-0.029	16.879	2100	2100
541	5420.77	2202.45	39.24	-0.11	16.937	2100	2100
542	5430.38	2202.42	39.31	-0.04	16.918	2100	2100
543	5441.14	2209.28	39.31	-0.082	16.831	2100	2100
544	5450.75	2209.22	39.38	-0.068	16.433	2100	2100
545	5460.37	2236.79	39.45	-0.022	16.349	2100	2100
546	5471.13	2230.39	39.38	-0.085	16.303	2100	2100
547	5480.74	2205.04	39.38	-0.057	16.006	2100	2100
548	5490.36	2186.44	39.45	-0.032	15.993	2100	2100

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A (mL·min^{-1})	Pump Flow B (mL·min^{-1})	Pump Pressure A (psi)	Pump Pressure B (psi)
549	5501.12	2206.30	39.45	-0.019	16.401	2100	2100
550	5510.73	2214.36	39.45	-0.034	16.744	2100	2100
551	5520.34	2217.01	39.45	-0.075	16.123	2100	2100
552	5531.17	2203.99	39.45	-0.033	16.259	2100	2100
553	5540.72	2212.62	39.45	-0.027	16.371	2100	2100
554	5550.33	2208.96	39.45	-0.02	16.024	2100	2100
555	5561.15	2198.80	39.60	-0.015	15.338	2100	2100
556	5570.71	2184.84	39.52	-0.025	16.119	2100	2100
557	5580.32	2207.42	39.52	-0.034	16.194	2100	2100
558	5591.14	2211.86	39.52	-0.045	15.623	2100	2100
559	5600.76	2212.79	39.67	-0.038	15.69	2100	2100
560	5610.31	2203.11	39.67	-0.03	15.742	2100	2100
561	5621.13	2183.73	39.52	-0.026	15.853	2100	2100
562	5630.75	2189.52	39.52	-0.057	15.317	2100	2100
563	5640.30	2219.62	39.67	-0.096	15.321	2100	2100
564	5651.12	2189.24	39.67	-0.018	15.62	2100	2100
565	5660.73	2201.37	39.67	-0.008	15.586	2100	2100
566	5670.29	2194.23	39.67	-0.014	15.39	2100	2100
567	5681.11	2193.08	39.67	-0.024	15.36	2100	2100
568	5690.72	2194.39	39.67	-0.081	15.638	2100	2100
569	5700.34	2200.90	39.74	-0.006	15.453	2100	2100
570	5711.10	2244.04	39.67	-0.003	15.328	2100	2100
571	5720.71	2206.85	39.67	-0.013	15.078	2100	2100
572	5730.33	2213.51	39.67	-0.051	15.562	2100	2100
573	5741.09	2200.00	39.74	0	15.89	2100	2100
574	5750.70	2207.81	39.74	-0.009	15.505	2100	2100
575	5760.31	2219.43	39.74	-0.027	15.305	2100	2100
576	5771.08	2182.50	39.67	-0.077	15.439	2100	2100
577	5780.69	2210.11	39.67	0	15.532	2100	2100
578	5790.30	2208.60	39.74	-0.016	15.259	2100	2100
579	5801.12	2226.56	39.74	0	15.186	2100	2100
580	5810.68	2216.31	39.81	-0.019	15.183	2100	2100
581	5820.29	2212.87	39.81	0	15.225	2100	2100
582	5831.11	2212.27	39.81	-0.014	15.176	2100	2100
583	5840.67	2193.08	39.67	-0.009	14.7	2100	2082
584	5850.28	2219.40	39.60	0	17.09	2100	2100
585	5861.10	2220.88	39.81	0	14.988	2100	2100
586	5870.71	2221.01	39.81	0	15.44	2100	2100
587	5880.27	2231.40	39.74	0	15.707	2100	2100
588	5891.09	2174.97	39.67	0	26.23	2100	2100
589	5900.70	2201.95	39.74	0	24.874	2100	2100
590	5910.26	2195.23	39.67	0	21.618	2100	2100
591	5921.19	2210.14	39.74	-0.03	20.291	2100	2100
592	5930.80	2199.32	39.74	0	22.551	2100	2090
593	5940.36	2171.79	39.67	0	29.385	2100	2092
594	5951.18	2183.28	39.60	0	27.319	2100	2100
595	5960.79	2158.42	39.74	0	27.394	2100	2100

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A ($mL \cdot min^{-1}$)	Pump Flow B ($mL \cdot min^{-1}$)	Pump Pressure A (psi)	Pump Pressure B (psi)
596	5970.35	2186.57	39.67	0	26.935	2100	2100
597	5981.17	2165.16	39.74	0	25.84	2100	2100
598	5990.78	2186.41	39.74	0	26.459	2100	2100
599	6000.39	2179.80	39.74	-0.023	26.616	2100	2100
600	6011.16	2163.79	39.74	-0.002	25.926	2100	2100
601	6020.77	2203.15	39.81	0	22.429	2100	2100
602	6030.38	2184.33	39.89	0	21.844	2100	2100
603	6041.15	2201.25	39.89	0	21.736	2100	2100
604	6050.76	2197.66	39.89	0	21.409	2100	2100
605	6060.37	2197.85	39.89	0	21.036	2100	2100
606	6071.14	2209.37	39.89	0	21.178	2100	2100
607	6080.75	2197.81	39.81	0	21.057	2100	2100
608	6090.36	2206.77	39.96	0	21.461	2100	2100
609	6101.13	2192.33	39.96	0	20.615	2100	2100
610	6110.74	2195.51	39.96	0	19.551	2100	2100
611	6120.35	2204.12	39.96	-0.046	19.51	2100	2100
612	6131.17	2192.02	39.89	0	19.742	2100	2100
613	6140.73	2217.66	39.96	0	19.407	2100	2100
614	6150.34	2208.44	39.89	0	19.289	2100	2100
615	6161.16	2198.57	39.96	0.263	16.656	2100	2073
616	6170.72	2210.07	39.81	-0.517	20.987	2100	2100
617	6180.33	2205.40	39.96	-0.01	19.564	2100	2100
618	6191.15	2218.84	39.89	-0.18	19.25	2100	2100
619	6200.76	2200.68	39.96	0.841	20.173	2100	2100
620	6210.32	2214.24	39.89	0.099	19.524	2100	2100
621	6221.14	2219.40	39.96	0	19.491	2100	2100
622	6230.75	2197.92	39.96	0	19.223	2100	2100
623	6240.31	2199.62	39.96	-0.717	19.218	2100	2100
624	6251.13	2206.04	39.96	0.082	19.112	2100	2100
625	6260.74	2200.74	39.89	0	19.389	2100	2100
626	6270.35	2202.14	39.89	0	19.234	2100	2100
627	6281.12	2208.08	39.81	-0.109	18.659	2100	2100
628	6290.73	2213.19	39.96	0.007	18.518	2100	2100
629	6300.34	2212.53	39.96	0	19.403	2100	2100
630	6311.11	2208.03	39.89	-0.057	19.117	2100	2100
631	6320.72	2224.51	39.89	-0.082	18.866	2100	2100
632	6330.33	2201.88	39.96	-0.002	18.314	2100	2100
633	6341.10	2216.22	39.96	-0.008	19.071	2100	2100
634	6350.71	2230.75	39.96	-0.089	8.295	2100	2073
635	6360.32	2194.48	39.81	0	20.211	2100	2100
636	6371.14	2249.22	39.96	-0.015	18.65	2100	2100
637	6380.70	2190.18	39.89	-0.025	18.184	2100	2100
638	6390.31	2205.69	39.89	-0.017	17.777	2100	2100
639	6401.13	2216.63	39.89	-0.014	17.601	2100	2100
640	6410.69	2224.29	39.96	-0.115	17.936	2100	2100
641	6420.30	2196.96	39.96	-0.053	17.925	2100	2100
642	6431.12	2172.92	39.96	-0.06	20.039	2100	2100

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A (mL·min^{-1})	Pump Flow B (mL·min^{-1})	Pump Pressure A (psi)	Pump Pressure B (psi)
643	6440.68	2192.07	39.96	1.255	0	2085	2054
644	6450.29	2181.87	39.67	19.822	0	2100	2066
Refill pump B, run pump A							
645	6461.11	2195.11	39.89	17.308	-204.169	2100	781
646	6470.72	2183.50	39.89	17.285	-204.047	2100	780
647	6480.28	2168.72	39.89	17.107	-203.89	2100	781
648	6491.10	2174.08	39.89	16.656	-204.062	2100	776
649	6500.71	2186.73	39.89	16.962	-203.849	2100	776
650	6510.27	2194.48	39.89	17.16	-204.10	2100	777
651	6521.09	2182.57	39.81	17.178	-203.50	2100	777
652	6530.70	2180.92	39.81	16.583	-204.05	2100	777
653	6540.31	2163.65	39.81	16.602	-204.08	2100	777
654	6551.08	2180.63	39.89	16.623	-204.08	2100	777
655	6560.69	2186.47	39.89	3.246	-204.06	2078	777
656	6570.30	2176.08	39.81	19.944	-204.08	2100	777
657	6581.07	2180.17	39.89	17.149	-204.08	2100	777
658	6590.68	2177.52	39.81	16.954	-204.07	2100	776
659	6600.29	2159.14	39.89	17.137	-204.09	2100	776
660	6611.06	2186.88	39.89	17.504	0	2100	784
Run pump B							
661	6620.67	2183.53	39.89	17.997	196.927	2100	867
662	6630.28	2183.29	39.81	18.67	195.98	2100	971
663	6641.10	2189.90	39.89	17.907	193.293	2100	1241
664	6650.66	2170.93	39.81	17.756	65.331	2100	1867
665	6660.27	2195.32	39.89	17.957	31.566	2100	2037
666	6671.09	2183.34	39.89	-1.548	37.932	2100	2091
667	6680.65	2193.40	39.96	-0.699	32.129	2100	2100
668	6690.26	2179.35	39.96	-0.383	28.213	2100	2100
669	6701.08	2191.03	39.96	-0.429	26.307	2100	2100
670	6710.64	2191.61	39.96	-0.249	25.616	2100	2100
671	6720.25	2200.71	39.96	-0.071	24.674	2100	2100
672	6731.07	2170.85	39.96	-0.163	24.556	2100	2100
673	6740.68	2212.50	39.89	-0.141	23.539	2100	2100
674	6750.24	2198.82	39.89	-0.148	23.35	2100	2100
675	6761.06	2180.32	39.74	2.876	22.623	2100	2089
676	6770.67	2199.52	39.89	-0.612	24.712	2100	2100
677	6780.23	2193.24	39.96	-0.795	23.309	2100	2100
678	6791.05	2196.28	39.89	-0.018	23.267	2100	2100
679	6800.66	2202.39	39.89	-0.041	22.622	2100	2100
680	6810.27	2193.46	39.89	-0.091	22.665	2100	2100
681	6821.04	2200.06	39.89	-0.704	22.434	2100	2100
682	6830.65	2184.96	39.81	-0.166	22.017	2100	2100
683	6840.26	2198.80	39.96	-0.065	21.417	2100	2100
684	6851.02	2203.24	39.89	-0.077	21.266	2100	2100
685	6860.64	2195.80	39.89	-0.105	21.371	2100	2100
686	6870.25	2189.41	39.89	-0.133	21.217	2100	2100
687	6881.01	2188.84	39.89	-0.151	21.259	2100	2100

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A (mL·min^{-1})	Pump Flow B (mL·min^{-1})	Pump Pressure A (psi)	Pump Pressure B (psi)
688	6890.63	2192.50	39.89	-0.053	21.302	2100	2100
689	6900.24	2200.28	39.89	-0.081	20.841	2100	2100
690	6911.06	2205.38	39.89	-0.092	20.394	2100	2100
691	6920.62	2203.43	39.96	0	20.341	2100	2100
Stop, refill, and run pump A, pump B continues running							
692	6930.23	2216.82	39.96	-203.96001	20.422	783	2100
693	6941.05	2196.55	39.89	-204.036	19.775	787	2100
694	6950.71	2229.23	39.89	-203.983	20.094	786	2100
695	6960.33	2184.57	39.96	-204.062	20.064	782	2100
696	6971.15	2208.94	39.96	-204.093	20.531	783	2100
697	6980.70	2193.79	39.89	-204.06599	20.73	783	2100
698	6990.32	2196.02	39.96	-204.03999	20.547	783	2100
699	7001.14	2218.29	39.89	-204.127	19.717	783	2100
700	7010.69	2199.52	39.96	-204.07401	19.843	783	2100
701	7020.31	2187.99	40.03	197.411	19.673	832	2100
702	7031.13	2191.71	39.89	195.976	19.865	966	2100
703	7040.74	2202.51	39.96	194.077	20.037	1203	2100
704	7050.29	2207.24	39.89	55.384	19.714	1893	2100
705	7061.11	2165.93	39.96	24.857	19.402	2082	2100
706	7070.89	2213.06	39.89	12.762	19.398	2100	2100
707	7080.50	2181.36	39.96	8.493	19.853	2100	2100
708	7090.12	2198.98	39.89	6.868	19.954	2100	2100
709	7100.88	2200.20	39.89	5.452	19.558	2100	2100
710	7110.49	2220.32	39.89	4.614	19.175	2100	2100
711	7120.10	2193.16	39.89	3.927	19.631	2100	2100
712	7130.87	2218.83	39.89	3.393	19.9	2100	2100
713	7140.48	2205.56	39.96	3.009	19.53	2100	2100
714	7150.09	2196.61	39.96	2.714	19.436	2100	2100
715	7160.91	2203.27	39.96	2.432	19.538	2100	2100
716	7170.47	2204.90	39.96	2.242	19.634	2100	2100
717	7180.08	2204.52	39.96	2.076	19.35	2100	2100
718	7190.90	2195.30	39.96	1.924	19.302	2100	2100
719	7200.46	2211.47	39.81	1.778	19.453	2100	2100
720	7210.07	2196.02	39.96	1.674	19.55	2100	2100
721	7220.89	2200.28	39.89	1.579	19.355	2100	2100
722	7230.51	2219.15	39.96	1.505	19.284	2100	2100
723	7240.06	2197.28	39.89	1.434	19.381	2100	2100
724	7250.88	2212.29	39.96	1.346	19.144	2100	2100
725	7260.49	2197.00	39.89	1.302	18.931	2100	2100
726	7270.05	2189.30	39.96	1.227	18.79	2100	2100
727	7280.87	2206.07	39.89	1.175	19.057	2100	2100
728	7290.48	2224.57	39.96	1.149	18.899	2100	2100
729	7300.10	2209.12	40.03	1.093	18.925	2100	2100
730	7310.86	2242.25	39.96	1.046	18.64	2100	2100
731	7320.47	2190.53	39.89	0.996	18.839	2100	2100
732	7330.08	2178.49	39.89	0.967	18.41	2100	2079
733	7340.85	2204.52	39.96	0.928	19.708	2100	2100

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A $(\mathrm{mL{\cdot}min^{-1}})$	Pump Flow B $(\mathrm{mL{\cdot}min^{-1}})$	Pump Pressure A (psi)	Pump Pressure B (psi)
734	7350.46	2206.55	39.96	1.016	19.238	2100	2100
735	7360.07	2191.83	39.89	0.88	18.74	2100	2100
736	7370.84	2196.69	39.89	0.828	19.071	2100	2100
737	7380.45	2198.20	39.96	0.794	19.084	2100	2100
738	7390.06	2226.31	39.96	0.748	19.286	2100	2100
739	7400.83	2208.62	39.96	0.709	19.032	2100	2100
740	7410.44	2196.87	39.96	0.708	18.574	2100	2100
741	7420.05	2203.04	39.96	0.68	18.843	2100	2100
742	7430.87	2199.71	39.89	0.644	18.959	2100	2100
743	7440.43	2197.00	39.89	0.624	19.036	2100	2100
744	7450.04	2174.30	39.89	0.599	19.262	2100	2100
745	7460.86	2210.96	40.03	0.586	19.259	2100	2100
746	7470.42	2207.17	39.96	0.585	18.819	2100	2100
747	7480.03	2207.56	40.03	0.557	18.813	2100	2100
748	7490.85	2208.03	39.96	0.527	19.179	2100	2100
749	7500.46	2212.43	39.96	0.5	19.433	2100	2100
750	7510.13	2204.93	39.96	0.498	19.068	2100	2100
751	7520.95	2214.52	39.89	0.487	18.873	2100	2100
752	7530.56	2202.79	39.96	0.461	18.828	2100	2100
753	7540.12	2200.96	39.96	0.461	19.233	2100	2100
754	7550.94	2210.49	39.96	0.433	19.393	2100	2100
755	7560.55	2196.31	39.96	0.415	19.183	2100	2100
756	7570.11	2195.04	39.89	0.414	18.704	2100	2100
757	7580.93	2211.84	39.96	0.398	19.134	2100	2100
758	7590.54	2209.31	39.96	0.386	19.329	2100	2100
759	7600.15	2222.64	39.96	0.377	18.997	2100	2100
760	7610.92	2175.89	39.89	0.343	19.277	2100	2100
761	7620.53	2205.06	39.96	0.348	18.934	2100	2100
762	7630.14	2225.86	39.96	0.342	18.78	2100	2100
763	7640.91	2210.05	39.96	0.332	19.167	2100	2100
764	7650.52	2220.04	39.96	0.212	19.795	2100	2100
765	7660.13	2191.57	39.96	0.362	19.39	2100	2100
766	7670.90	2226.68	39.96	0.325	18.996	2100	2100
767	7680.51	2207.83	40.03	0.303	19.415	2100	2100
768	7690.12	2202.25	39.96	0.305	19.682	2100	2100
769	7700.89	2205.97	39.96	0.298	19.905	2100	2100
770	7710.50	2203.26	39.89	0.274	20.296	2100	2100
771	7720.11	2205.88	39.96	0.258	19.755	2100	2100
772	7730.93	2215.97	39.89	0.247	19.899	2100	2100
773	7740.49	2184.96	40.03	0.248	19.901	2100	2100
774	7750.10	2207.70	40.03	0.245	20.074	2100	2100
775	7760.92	2191.99	39.96	0.233	20.148	2100	2100
776	7770.48	2203.37	39.96	0.227	19.812	2100	2100
777	7780.09	2232.93	39.89	0.226	19.759	2100	2100
778	7790.91	2205.23	39.96	0.221	20.106	2100	2100
779	7800.52	2202.89	39.89	0.216	20.629	2100	2100
780	7810.08	2168.03	39.60	20.321	0	2082	2031

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A (mL·min^{-1})	Pump Flow B (mL·min^{-1})	Pump Pressure A (psi)	Pump Pressure B (psi)
781	7820.90	2161.41	39.67	18.958	0	2100	2049
782	7830.51	2159.43	39.67	18.975	0	2100	2047
783	7840.07	2150.02	39.81	19.512	0	2100	2048
784	7850.89	2153.44	39.89	19.98	0	2100	2048
785	7860.50	2121.45	39.81	14.319	0	2073	2022
786	7870.11	2145.16	39.74	23.55	0	2100	2034
787	7880.88	2159.91	39.81	20.101	0	2100	2040
788	7890.49	2163.15	39.81	19.034	0	2100	2043
789	7900.10	2159.96	39.89	19.952	0	2100	2044
790	7910.87	2163.31	39.89	19.637	0	2100	2046
791	7920.48	2154.74	39.89	19.985	0	2100	2046
792	7930.09	2139.83	39.89	19.725	0	2100	2047
793	7940.86	2143.40	39.89	20.141	0	2100	2047
794	7950.47	2149.82	39.81	20.124	0	2100	2047
795	7960.08	2177.96	39.81	19.983	0	2100	2047
796	7970.85	2162.67	39.89	20.234	0	2100	2047
797	7980.46	2171.04	39.89	19.521	0	2100	2048
798	7990.07	2144.43	39.89	19.705	0	2100	2048
799	8000.89	2141.48	39.89	19.837	0	2100	2048
800	8010.45	2170.06	39.96	19.944	0	2100	2048
801	8020.06	2180.19	39.89	20.1	0	2100	2049
802	8030.88	2177.90	39.96	19.508	0	2100	2049
803	8040.44	2163.72	39.96	19.798	0	2100	2049
804	8050.05	2148.59	39.96	19.942	0	2100	2049
805	8060.98	2157.88	39.89	19.425	0	2100	2049
806	8070.54	2160.79	39.89	19.739	0	2100	2050
807	8080.15	2147.89	39.89	19.565	0	2100	2050
808	8090.97	2128.84	39.96	19.53	0	2100	2050
809	8100.52	2184.59	39.96	19.689	0	2100	2050
810	8110.14	2163.31	40.03	19.602	0	2100	2051
811	8120.96	2165.77	39.89	19.599	0	2100	2051
812	8130.57	2175.37	39.96	19.72	0	2100	2051
813	8140.13	2137.51	39.89	19.699	0	2100	2051
814	8150.95	2163.65	39.96	19.559	0	2100	2052
815	8160.56	2161.64	39.89	20.028	0	2100	2052
816	8170.12	2157.28	39.89	19.787	0	2100	2052
817	8180.94	2171.46	39.96	19.373	0	2100	2052
818	8190.55	2195.87	39.96	19.125	0	2100	2053
819	8200.16	2164.67	40.03	18.468	0	2100	2053
820	8210.93	2168.36	39.96	18.295	0	2100	2053
821	8220.54	2151.69	40.03	17.764	0	2100	2054
822	8230.15	2166.20	40.03	17.89	0	2100	2054
823	8240.91	2183.76	39.89	17.446	0	2100	2054
824	8250.53	2181.46	39.81	17.344	0	2100	2054
825	8260.14	2173.15	39.96	17.483	0	2100	2054
826	8270.90	2174.14	40.03	17.711	0	2100	2055
827	8280.52	2167.21	40.03	17.717	0	2100	2055

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A ($mL \cdot min^{-1}$)	Pump Flow B ($mL \cdot min^{-1}$)	Pump Pressure A (psi)	Pump Pressure B (psi)
828	8290.13	2160.26	39.96	17.344	0	2100	2055
829	8300.95	2179.31	39.96	17.331	0	2100	2055
830	8310.51	2176.90	40.03	17.393	0	2100	2055
831	8320.12	2160.67	40.03	17.625	0	2100	2056
832	8330.94	2202.26	40.03	17.607	0	2100	2056
833	8340.49	2162.40	39.96	18.734	0	2085	2038
834	8350.11	2171.19	39.89	17.851	0	2100	2046
835	8360.93	2148.57	39.96	17.46	0	2100	2050
836	8370.48	2161.99	40.03	17.723	0	2100	2052
837	8380.10	2189.03	39.89	17.628	0	2100	2054
838	8390.92	2178.27	39.89	17.377	0	2100	2055
839	8400.53	2181.42	39.96	17.027	0	2100	2055
840	8410.08	2166.20	39.89	17.319	0	2100	2056
841	8420.91	2180.35	39.96	17.422	0	2100	2056
842	8430.52	2167.60	39.96	17.733	0	2100	2057
843	8440.07	2191.13	39.89	17.592	0	2100	2057
844	8450.89	2195.38	40.03	16.937	0	2100	2057
845	8460.51	2184.04	39.96	17.018	0	2100	2058
846	8470.12	2179.47	40.03	17.192	0	2100	2058
847	8480.88	2153.51	39.96	17.351	0	2100	2058
848	8490.50	2191.60	39.96	17.305	0	2100	2058
849	8500.11	2186.60	39.96	16.979	0	2100	2059
850	8510.87	2163.66	39.96	17.038	0	2100	2059
851	8520.49	2137.54	39.96	17.192	0	2100	2059
852	8530.10	2166.58	39.96	17.41	0	2100	2059
853	8540.86	2185.00	39.96	17.365	0	2100	2059
854	8550.47	2177.62	39.96	17.043	0	2100	2059
855	8560.09	2157.11	40.03	16.948	0	2100	2059
End of extraction, pressure decrease in vessel							
856	8570.91	2068.43	39.60	-0.89	0	2100	2065
857	8580.46	1928.47	38.88	-0.555	0	2100	2069
858	8590.08	1699.60	37.69	-0.32	0	2100	2069
859	8600.90	1515.37	35.69	-0.382	0	2100	2069
860	8610.45	1434.95	34.98	-0.176	0	2100	2069
861	8620.07	1374.73	35.05	-0.206	0	2100	2069
862	8630.89	1352.48	35.24	-0.205	0	2100	2069
863	8640.50	1325.08	35.37	-0.106	0	2100	2068
864	8650.05	1320.26	35.56	-0.152	0	2100	2067
865	8660.87	1310.67	35.75	-0.163	0	2100	2066
866	8670.49	1298.13	35.95	-0.087	0	2100	2065
867	8680.04	1270.88	36.15	-0.056	0	2100	2064
868	8690.86	1299.10	36.21	-0.13	0	2100	2063
869	8700.48	1278.52	36.21	-0.05	0	2100	2063
870	8710.03	1281.53	36.28	-0.044	0	2100	2063
871	8720.85	1240.24	36.34	-0.063	0	2100	2063
872	8730.47	1277.05	36.28	-0.022	0	2100	2063
873	8740.08	1287.11	36.28	-0.13	0	2100	2063

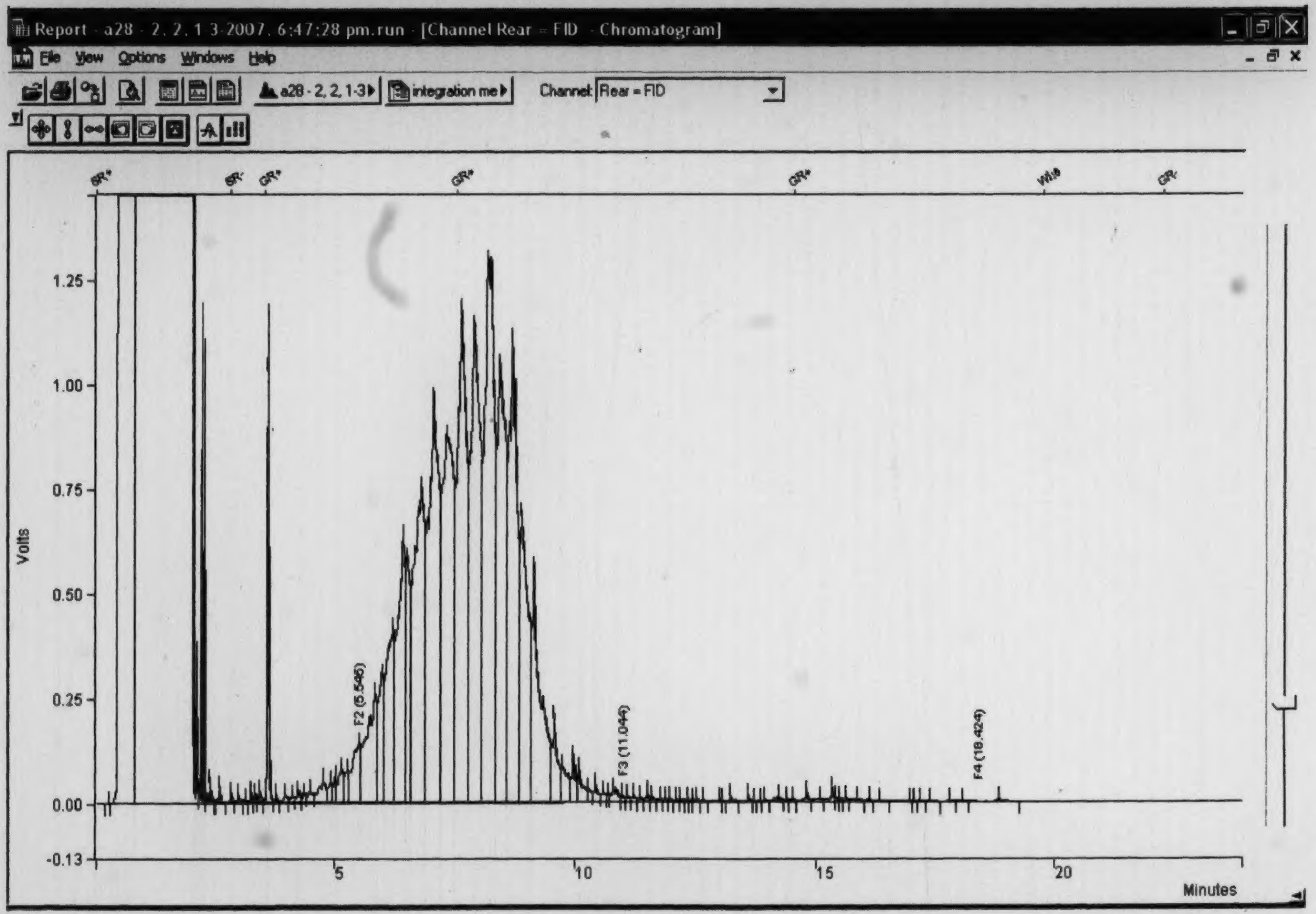
No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A ($mL\cdot min^{-1}$)	Pump Flow B ($mL\cdot min^{-1}$)	Pump Pressure A (psi)	Pump Pressure B (psi)
874	8750.84	1278.40	36.15	-0.052	0	2100	2063
875	8760.45	1248.46	36.15	-0.055	0	2100	2063
876	8770.07	1253.79	36.08	-0.057	0	2100	2063
877	8780.83	1213.97	36.02	-0.046	0	2100	2063
878	8790.44	1274.55	35.95	-0.049	0	2100	2063
879	8800.17	1235.83	35.88	-0.088	0	2100	2063
880	8810.93	1218.57	35.56	-0.109	0	2100	2063
881	8820.54	1205.80	35.49	-0.002	0	2100	2063
882	8830.16	1183.67	35.43	-0.014	0	2100	2063
883	8840.92	1182.04	35.24	-0.015	0	2100	2063
884	8850.53	1167.45	35.17	-0.04	0	2100	2063
885	8860.14	1171.07	34.98	-0.04	0	2100	2063
886	8870.91	1119.32	34.79	-0.001	0	2100	2063
887	8880.52	1098.59	34.73	-0.033	0	2100	2063
888	8890.13	1103.42	34.60	0	0	2100	2063
889	8900.95	1051.35	34.48	-0.008	0	2100	2063
890	8910.51	1020.07	34.35	-0.006	0	2100	2063
891	8920.12	981.75	34.22	-0.011	0	2100	2063
892	8930.94	990.75	34.16	0	0	2100	2063
893	8940.50	955.65	34.22	-0.014	0	2100	2063
894	8950.11	908.73	34.04	0	0	2100	2063
895	8960.93	921.56	33.85	-0.041	0	2100	2063
896	8970.54	846.09	33.79	-0.007	0	2100	2063
897	8980.10	814.47	33.48	0	0	2100	2063
898	8990.92	761.54	33.12	0	0	2100	2063
899	9000.53	722.11	32.87	-0.018	0	2100	2063
900	9010.09	674.00	32.69	0	0	2100	2063
901	9020.91	664.61	32.69	0	0	2100	2063
902	9030.52	590.19	32.75	-0.037	0	2100	2063
903	9040.14	551.85	32.81	0.018	0	2100	2063
904	9050.90	529.12	32.93	0	0	2100	2062
905	9060.51	530.36	33.06	0	0	2100	2062
906	9070.12	471.20	33.24	0	0	2100	2062
907	9080.89	455.16	33.42	0	0	2100	2063
908	9090.50	420.63	33.60	0	0	2100	2063
909	9100.11	405.72	33.73	0	0	2100	2063
910	9110.88	393.34	33.98	0	0	2100	2063
911	9120.49	394.48	34.10	0	0	2100	2063
912	9130.10	366.09	34.29	0	0	2100	2063
913	9140.87	348.65	34.48	0	0	2100	2063
914	9150.48	315.07	34.60	0	0	2100	2063
915	9160.09	289.53	34.79	0	0	2100	2063
916	9170.91	284.81	35.05	0	0	2100	2064
917	9180.47	289.70	35.17	0	0	2100	2063
918	9190.08	271.63	35.24	0	0	2100	2063
919	9200.90	214.66	35.49	0	0	2100	2063
920	9210.46	292.79	35.56	0	0	2100	2064

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A (mL·min^{-1})	Pump Flow B (mL·min^{-1})	Pump Pressure A (psi)	Pump Pressure B (psi)
921	9220.07	241.80	35.69	0	0	2100	2063
922	9230.89	245.45	35.82	0	0	2100	2063
923	9240.50	226.25	35.95	0	0	2100	2063
924	9250.06	208.71	36.08	0	0	2100	2063
925	9260.88	217.08	36.08	0	0	2100	2063
926	9270.49	214.32	36.21	0	0	2100	2063
927	9280.05	242.62	36.34	0	0	2100	2063
928	9290.87	193.83	36.48	0	0	2100	2063
929	9300.48	213.66	36.48	0	0	2100	2063
930	9310.15	187.50	36.54	0	0	2100	2063
931	9320.97	193.33	36.61	0	0	2100	2063
932	9330.58	132.63	36.74	0	0	2100	2063
933	9340.14	163.84	36.81	0	0	2100	2062
934	9350.96	165.97	36.88	0	0	2100	2062
935	9360.57	177.38	37.01	76.348	0	1873	1804
936	9370.18	166.11	37.01	22.261	0	1872	1838
937	9380.95	219.36	37.42	91.939	0	1841	1780
938	9390.56	251.53	38.60	1.506	0	2100	1805
939	9400.17	265.30	39.52	-0.223	0	2100	1814
940	9410.94	283.49	39.67	0	0	998	993
941	9420.55	285.18	39.67	0	0	1197	1084
942	9430.16	272.45	39.52	0	0	1284	1105
943	9440.93	295.39	39.31	0	0	1340	1117
944	9450.54	237.85	39.16	0	0	1371	1124
945	9460.15	253.54	39.02	0	0	1393	1130
946	9470.97	267.76	38.74	0	0	1408	1136
947	9480.53	246.55	38.60	0	0	1421	1141
948	9490.14	310.17	38.53	0	0	1429	1146
949	9500.96	243.50	38.39	0	0	1438	1151
950	9510.52	268.74	38.32	0	0	1444	1155
951	9520.13	239.46	38.18	0	0	1448	1159
952	9530.95	262.18	38.11	0	0	1454	1164
953	9540.51	258.11	38.04	0	0	1458	1168
954	9550.12	252.17	37.97	0	0	1461	1172
955	9560.94	251.78	37.97	0	0	1465	1177
956	9570.55	286.71	37.76	0	0	1468	1181
957	9580.11	264.89	37.76	0	0	1469	1185
958	9590.93	214.15	37.69	0	0	1471	1189
959	9600.54	304.54	37.62	0	0	1474	1193
960	9610.10	215.19	37.55	0	0	1476	1197
961	9620.92	292.94	37.49	0	0	1477	1201
962	9630.53	224.40	37.42	0	0	1479	1205
963	9640.14	232.29	37.42	0	0	1480	1208
964	9650.91	256.67	37.42	0	0	1482	1213
965	9660.52	222.86	37.28	0	0	1484	1216
966	9670.13	228.11	37.28	0	0	1485	1219
967	9680.90	316.19	37.28	0	0	1489	1223

No.	Time (sec)	Vessel Pressure (psi)	Vessel Temperature (°C)	Pump Flow A (mL·min^{-1})	Pump Flow B (mL·min^{-1})	Pump Pressure A (psi)	Pump Pressure B (psi)
968	9690.51	229.63	37.28	0	0	1493	1226
969	9700.12	217.44	37.28	0	0	1497	1230
970	9710.89	245.83	37.15	0	0	1501	1233
971	9720.50	212.29	37.15	0	0	1505	1237
972	9730.11	225.92	37.08	0	0	1509	1240

APPENDIX B - SAMPLE GC/FID RESULTS OUTPUT

```
Title       :
Run File    : c:\star\a28 - 2, 2, 1-3-2007, 6;47;28 pm.run
Method File : d:\documents and settings\cstreet\my documents\experimental
data\gc methods\methods - nov 2006\integration method samples - nov 2006.mth
Sample ID   : a28 - 2

Injection Date: 1/3/2007 7:47 PM    Calculation Date: 1/4/2007 1:47 PM

Operator    : Nick                  Detector Type: 3800 (10 Volts)
Workstation: Local Disk             Bus Address  : 44
Instrument : 3800GC                 Sample Rate  : 10.00 Hz
Channel     : Rear = FID            Run Time     : 23.977 min

** Star Chromatography Workstation (Demo) Version 5.50 ** 05000-1A68-DA2-3be9
**

Run Mode          : Analysis
Peak Measurement: Peak Area
Calculation Type: Percent

                                Ret.    Time                       Width
 Peak      Peak        Result   Time   Offset      Area     Sep.   1/2    Status
  No.      Name          ()     (min)  (min)     (counts)   Code  (sec)   Codes
 ---- ------------ ----------  ------- ------- ----------   ----  -----   ------
    1 F2              41.2081    5.545  -0.054   69011752    GR    0.0
    2 F3              58.0335   11.044  -0.063   97189344    GR    0.0
    3 F4               0.5256   18.424  -0.174     880228    GR    0.0
 ---- ------------ ==========  ------- ======= ==========   ----  -----   ------
      Totals:         99.7672           -0.291  167081324

Total Unidentified Counts :      389836 counts

Detected Peaks: 84          Rejected Peaks: 0      Identified Peaks: 3

Multiplier: 1          Divisor: 1          Unidentified Peak Factor: 0

Baseline Offset: -174 microVolts

Noise (used): 100 microVolts - fixed value
Noise (monitored before this run): 385 microVolts

Vial: 6        Injection Number: 2     Volume: 2.0  uL     Position: 1

********************************************************************************
```


Report - a28 - 2. 2. 1-3-2007. 6:47:28 pm.run - [Channel Rear = FID - Chromatogram]
File View Options Windows Help
a28 - 2, 2, 1-3
integration me
Channel: Rear = FID
GR*
GR-
GR*
GR*
GR*
WI-9
GR-
Volts
1.25
1.00
0.75
0.50
0.25
0.00
-0.13
F2 (5.546)
F3 (11.044)
F4 (18.424)
5
10
15
20
Minutes